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Technical Report for the Period 1. 10. 59 to 30. 6. 60

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1. ~~Packaging materials~~
2. ~~Plastics~~
3. ~~Solid propellants~~
4. ~~Liquid propellants~~
5. ~~Internal ballistics~~
6. ~~Explosives - Initiation~~
7. ~~Explosives~~ ~~Initiating compositions~~
8. ~~Chemistry~~

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TECHNICAL REPORT

FOR THE PERIOD

1.10.1959 to 30.6.1960 4

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CONTENTS

		Page No.
I	FIBRES (TEXTILES)	1
I.1	Basic Fibre Properties	1
I.4	Flame and Radiant Heat Protection	1
IV	PACKAGING MATERIALS	3
IV.2	Barrier Materials	3
IV.3	Cushioning Materials	3
IV.4	Desiccants	3
IV.5	Inhibitors	4
IV.6	Advice on Materials	4
V	PLASTICS	5
V.1	Armaments	5
V.4	Electrical, Electronics, Radar and Radio	6
V.6	Materials (Including New Polymers) and Properties	6
VI	RUBBERS	10
VI.1	Armaments	10
VI.5	Engineers Equipment	10
VI.6	Materials and Properties	12
VII	ADHESIVES, SEALING COMPOSITIONS AND VARNISHES	14
VII.2	Adhesion	14
VII.3	Sealing Compositions	14
VII.4	Varnishes	15
XX	SOLID ROCKET CHARGES	17
XX.4	Inspection Methods	17
XXI	SOLID PROPELLANTS FOR ROCKETS	18
XXI.1	Colloidal Propellants - Extruded	18
XXI.2	Colloidal Propellants - Cast	21
XXI.3	Plastic Propellants	28
XXI.4	Polyurethane Propellants	30
XXI.6	Composite Propellants	38
XXII	PROPELLANTS FOR ORDNANCE	42
XXII.1	New Equipments	42
XXIII	PROPELLANTS FOR SMALL ARMS	44
XXIII.2	Ball Powder	44

/CONTENTS contd. .....

CONTENTS (contd.)

	Page No.
XXIV LIQUID PROPELLANTS	46
XXIV.1 Hydrogen Peroxide	46
XXV INTERNAL BALLISTICS RESEARCH	48
XXV.2 Experimental Studies on Flame Propagation and Combustion Mechanisms	48
XXV.3 Solid Systems	49
XXVI SENSITIVENESS AND DETONABILITY OF PROPELLANTS, HIGH EXPLOSIVES AND INITIATORS	54
XXVI.1 Evaluation of the Sensitiveness of Explosives and Propellants	54
XXVI.2 Fundamental Studies of Explosive Initiation Phenomena	55
XXVI.3 Explosive Hazards	56
XXVI.4 Evaluation of the Sensitiveness of Initiators	58
XXVII CHEMISTRY OF PROPELLANT INGREDIENTS	60
XXVII.1 Nitrocellulose	60
XXVII.2 Boranes	62
XXVIII CHEMISTRY OF HIGH EXPLOSIVES	65
XXVIII.1 TNT	65
XXVIII.3 Other Explosives	67
XXIX CHEMISTRY OF INITIATORS	69
XXIX.1 L.D.N.R. and Other Lead and Barium Salts of Nitrophenols	69
XXIX.3 Other Materials for Initiator Compositions	69
XXXI CHEMICAL ENGINEERING	71
XXXI.1 Research	71
XXXI.2 Manufacturing Processes	74
XXXII ANALYTICAL CHEMISTRY	80
XXXII.1 Analysis	80
XXXII.2 Compatibility	81
XXXII.3 Stability	84
XXXII.4 Services to Branches	86
XXXII.5 Crystallography of Explosives, Propellants and Initiators	90
XXXIII PYROTECHNIC COMPOSITIONS	93
LIST OF REPORTS ISSUED	94 - 97
List of D.M.X.R.D. Reports Issued	98

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I FIBRES (TEXTILES)

I.1 BASIC FIBRE PROPERTIES

The Cross-linking of Cellulose: Extra Mural Research Contract with the British Rayon Research Association

The aim of the investigation is to introduce specific cross-linkages into cellulose and if possible to determine the number of cross-linkages produced. By so doing it is hoped to gain knowledge whereby cellulose and its derivatives can be made more durable and, in particular, more resistant to heat.

The method used has consisted in the preparation of crotonyl derivatives of cellulose, which, when reacted with ethylenediamine, have been made to undergo cross-linking, the diamine adding on to the double bonds of the crotonyl groups. The physical properties of films made from the products of these reactions are being studied.

The Effect of Metallic Oxides on the Photochemical Degradation of Cellulose

Various metallic compounds are used in the treatment of cotton textiles for such purposes as colouration, preservation, flame-resistance, etc., and are so used very extensively in Service stores. Some of these additives are known to influence the degradation of cellulose on exposure to sunlight, and the way in which these reactions occur and the rates at which they proceed are the subject of this investigation.

Purified cotton cellulose has been impregnated with copper oxide, cuprammonium hydroxide, and copper sulphate, to yield copper contents between 0.1 per cent and 1.0 per cent of copper, and samples of these materials are undergoing exposure to daylight in glass frames. Preparations are being made for the treatment of cellulose with other metallic oxides and for the exposures to include irradiation from a xenon arc.

Results obtained so far indicate that the degradation of cellulose by daylight is accelerated by the presence of copper oxide and it has also been observed that prolonged exposure in the open air results in the formation of copper sulphate, caused presumably by traces of sulphur dioxide in the atmosphere.

I.4 FLAME AND RADIANT HEAT PROTECTION

The Response of Non-metallic Materials to the Effects of High Intensity Thermal Radiation

This investigation consists of a survey of the behaviour of non-metallic materials, textiles in particular, when exposed to an intense source of radiant heat, intended to simulate the heat effects of a nuclear explosion. Particular attention is being given to the rate and nature of breakdown and to the transmission of heat through the material. Experiments are being carried out (i) to determine the rate of strength loss at known levels of heat flux, (ii) on the effects of enhancing the reflectivity of the material,

/(iii) .....

(iii) on the effect of additives such as proofings and coatings, and (iv) on the transmission of heat through single and multiple layers of fabric. The work done so far has mainly been the development of test techniques, measurement of the heat flux, and attempts to establish a relationship between tests done in the laboratory and those carried out in the field. Some uncertainty still exists regarding the quantitative intensity of heat being developed by the apparatus but the indications are that reasonable correlation can be obtained between field and laboratory tests.

/IV .....

IV PACKAGING MATERIALS

IV.2 BARRIER MATERIALS

IV.2.1 Bag Liners: Development of Liners with Better Performance

A trial by E.I.D. with wooden cases containing bag liners made from a polythene-coated creped Kraft has shown that this type of liner is unsuitable for full-standard Service packaging. No further work on this project is being planned.

IV.2.2 Low Temperature: Behaviour of Materials at Low Climatic Temperatures

A summary of available information has been prepared for Central Packaging Branch. No further work on this project is planned.

IV.2.3 Water-proofing: Treatment of Fibre-board to Increase Weather Resistance

A field trial is being carried out with the co-operation of War Office and Air Ministry. Fibre-board cases with dummy loads are being treated after closure with three types of water-proofing material before being submitted to the Schedule of Tests, DEF 1234, and to real journey hazards.

IV.3 CUSHIONING MATERIALS

Properties under Shock-loading Conditions

This E.M.R. contract with P.A.T.R.A. is ending in July 1960 and the final report is expected within six months. Specimens of rubberised hair and a cellular rubber drawn from a bulk supply have been sent to six laboratories possessing drop-hammer accelerometers similar to that at P.A.T.R.A. A method of test has been agreed by which the results from the six instruments can be compared.

IV.4 DESICCANTS

IV.4.1 Improvements in Desiccant Containers for Packaging

In co-operation with D.S.C.D., War Office, and Messrs Crosfields, a performance specification for silica gel containers has been written and the designing of new types of container to replace the current bags has begun.

/IV.4.2 .....

IV.4.2 Effect of Hygroscopic Dunnage on Relative Humidity in Desiccated Packs

The work under E.M.R. contract with P.A.T.R.A. continues. Examination of the behaviour of rubberised hair above temperate ambient temperatures is concluded. The two specimens of hygrometer have proved unsatisfactory and one based on dew-point measurement is being considered.

IV.5 Inhibitors

IV.5.1 The Use of Calcium Hydroxide to Prevent Rusting of Ferrous Metals

It is known that slaked lime can inhibit the rusting of ferrous metals, although the exact conditions necessary to achieve this are not known. As it is thought that this material may be of use in preserving ferrous metals under long-term storage, an E.M.R. contract has been placed with the Chalk, Lime and Allied Trades Research Association to examine the mechanism and the limitations of inhibition by calcium hydroxide under the conditions of Service packaging.

IV.5.2 The Relative Values of Fungicides Available for Application to Papers during Manufacture

Papers containing fungicides added during manufacture are not readily available commercially. Samples of papers have now been obtained to which copper-8-hydroxyquinolate, lauryl pentachlorophenol and Panacide (Dichlorphen) have been added; these will be examined at D.C.I.

IV.6 Advice on Materials

By agreement with the Central Packaging Branch a Technical Panel has been set up, under the chairmanship of S.M.R., to answer questions on new packaging materials and report on facilities for testing.

/V .....

V PLASTICS

V.1 ARMAMENTS

V.1.1 Ammunition

Development Of Nonmetallic Driving Bands For Projectiles

The success of the vulcanized fibre and nylon driving bands on 105 mm A.P.D.S. projectile has led to further interest in nonmetallic materials for this purpose. Driving bands are at present required for 120 mm A.P.D.S. and F.B.A. projectiles. For the former, Nylon 6 is being used and the difficulties in making porosity-free large mouldings have been overcome by using the new extrusion/injection type of machine. The 105 mm F.B.A. projectile requires a driving band that discards on leaving the gun, i.e., the band should break up. Two grades of high-impact polystyrene are being tried and seem promising. Most of the processing difficulties have been overcome and physical properties of the materials have been checked. Firing trials indicate that a gain of 5 per cent in range can be obtained using plastic bands made from these polystyrenes and further investigation is considered well worth while.

Effect of High Explosives on various Styrene Polymers and Co-polymers

Polystyrene (Lustrex G.P.), high-impact polystyrenes (Lustrex T3 and T11 and Styron 475) and a cross-linked polystyrene (Lucentine) are all unaffected after six months at 60°C in contact with either RDX/TNT or TNT. Acrylonitrile/butadiene/styrene (A.B.S.) co-polymers (Kralastic and Cycolac) show considerable weight increases after contact with either explosive, but no catastrophic deterioration in physical properties; the adhesion of explosive to polymer is such that it is impossible to remove the explosive completely from the specimen by mechanical means.

Antistatic Cloth (P.V.C.-Covered Nylon) in Contact with Casting Powders

Antistatic cloth is being investigated for a proposed use as bag material for casting powders. Cloth in contact with any one of the three casting powders used becomes very stiff after one month at 60°C and shows very appreciable weight loss but no loss in tensile strength. The loss of weight is probably due to plasticiser migration from the P.V.C. coating to the casting powder. A further and possibly more serious effect is the marked increase in electrical resistance of the cloth, to such an extent that it might no longer be regarded as antistatic.

V.1.4 Rockets

Resistance of Plastics to Isopropyl Nitrate

More work on the effect of isopropyl nitrate on nylons and polythenes is in progress. If I.P.N. is first treated with diphenylamine (proportions of 1 and 5 per cent by weight were used) both the nylons and polythenes will be protected from degradation due to contact with the I.P.N. In untreated I.P.N. a commercially stabilised nylon 6.6 was more resistant than unstabilised material, but it degraded quicker in untreated I.P.N. than unstabilised nylon 6.6 in treated I.P.N. Again a commercially stabilised

nylon .....

nylon 6 was little better than unstabilised nylon 6 in untreated I.P.N. It appears therefore that, while a stabiliser in the nylon may have some beneficial effect, a greater benefit is obtained if the stabiliser is in the I.P.N.

With polythenes the same effect as with nylons is noticed, i.e., if the I.P.N. is treated with diphenylamine it has no degrading effect on the polythenes within the time scale of the experiment.

V.4 ELECTRICAL, ELECTRONICS, RADAR AND RADIO

Dielectric Materials of High Softening Point: E.M.R. with Yarsley Research Laboratories

Several variations of the Ziegler catalyst system have been investigated and high yields of isotactic polystyrene obtained. High and low molecular weight material is being prepared in ½-lb quantities for full evaluation. This, and some atactic styrene derivatives, e.g. poly- α-vinyl naphthalene and poly di-isopropyl styrene, already meet the requirement for a dielectric material usable up to 150°C. To extend the range to 200°C and above, a number of styrene derivatives (poly- α-vinyl naphthalene, poly-2,5-dichlorostyrene, poly-3,4-dimethyl styrene, polyvinyl toluene and polyvinyl xylene) are being prepared in isotactic form. To begin with, 1 gram quantities only are being prepared to check their thermal stability.

The restriction of this work to styrene derivatives has been considered too limiting, and Yarsleys have put forward a number of proposals for other novel systems worth investigating. The applications of these materials would not necessarily be confined to the dielectric field.

Effect of High Temperature Aging on the Dielectric Properties of Polyethylene: E.M.R. with British Insulated Callenders Cables

By selecting a suitable carbon black and antioxidant and reducing the amount of carbon black to 1 per cent, a number of polythene compounds now have satisfactory high-frequency dielectric properties both before aging and after heat-aging at approximately 100°C for 5,000 hours. Further tests are being carried out in which the specimens are subjected to light-aging (xenon arc) at elevated temperatures (60° - 70°C) for 5,000 hours.

V.6 MATERIALS (INCLUDING NEW POLYMERS) AND PROPERTIES

V.6.1 New Polymers

Organoarsenical Polymers

Two new polymers have been synthesised:

Poly-9,10-anthracene phenylarsine (soluble in chloroform, softens at 270°C),

Poly-2,5-thiophene phenylarsine (soluble in benzene and chloroform, softens at 90°C)

Attempts to prepare regular copolymers by reacting mixtures of phenyldichloroarsine and organic dibromides with magnesium were not successful because arsenobenzene and its homopolymers were formed

/preferentially .....

preferentially.

The thermal stability values for all the polymers prepared so far indicate that those containing p-phenylene linkages are more stable than those containing m-phenylene linkages, which, in turn, are more stable than those with o-phenylene linkages.

Modified Polyphenylenes

The preparation and investigation of poly(9,10-anthracene)ethylene and poly(2,6-naphthalene)-ethylene have been continued.

A further series of polyoxides has been prepared by the decomposition of metal halogenophenoxides including poly(chlorophenylene) oxide, poly(bromophenylene) oxide, poly(2,5-dichlorophenylene)oxide, poly(2,3,5-trichlorophenylene) oxide, and poly(2,3,5,6-tetrabromophenylene) oxide, all of which have softening points in excess of 200°C. The formation of p-dibenzodioxins by ortho-elimination of metal halide has been observed as a competing reaction to polymer formation in some cases.

Testing of Polymers Using Small Quantities

Usually, on first synthesis, only a small amount of a polymer is available for assessment of its physical properties and mouldability. Therefore test methods using small specimens are required. For engineering design a knowledge of the effect of the alteration of testing technique on the magnitude of measured physical properties is necessary. A study of the effect in tensile and impact tests is being made with nylon 6.6, nylon 6.10 and polystyrene.

Measurement of Physical Properties of Polymers

The physical properties of new polymers and their variation over the temperature range -60° to +120°C are determined on behalf of Service departments as required. Materials recently tested include rubberised polystyrene, polypropylene and polycarbonate.

New Polymers based on Inorganic Elements: E.M.R. with Aberdeen University

Methods of preparation of materials containing silicon-nitrogen bonds in the main chain have shown that it is possible to prepare polymeric materials of this type with good thermal stability. Further work is being carried out on this system and it is intended to begin work on the silicon-phosphorus compounds.

V.6.2 Polymer Properties

Tensile Properties at High Rates of Strain

Investigations using the M.R.L. Tensile Impact Machine with nylon 6.6, cellulose acetate butyrate and plasticised polyvinyl chloride have been reported. Embrittlement of nylon 6.6, (tested at 230 inches/s) was determined as a function of moisture content, of cellulose acetate butyrate as a function of temperature and strain rate, and of polyvinyl chloride as a function of plasticiser content and strain rate.

/Following .....

Following preliminary small-scale experiments, the pendulum and striker of a 120 ft lb impact machine are being modified to accommodate tensile specimens. A crystal accelerometer will be used to record the variations of force with time during tensile impact at strain rates similar to those of the M.R.L. Tensile Impact Machine. It is hoped that the force/time records will show whether the hypothesis, that a limiting strength is associated with brittle fracture, is correct.

Results on polymethyl methacrylate over a wide range of strain rates have been taken from the literature and plotted as reciprocal (maximum yield stress) v. log (fracture time); a limiting strength is approached when the fracture time is in the region of 1 millisecond. However, no information is available on the form of fracture (ductile or brittle) at this stress.

Crystallization of High Polymers: E.M.R. with Bristol University

Investigations are in progress to test the validity of various theories relating to the phenomenon of folding in polymer chains during solidification. While no clear-cut answer has yet been obtained a number of novel crystallization effects have been noted, the most important of which is that the fold length is fully determined by the temperature at which the folds are formed and does not depend on the length of folds already present.

A number of apparently unusual crystal habits can now be obtained systematically and these are relevant to studies of folding behaviour.

The development of a new technique for the preparation of specimens for electron microscope work has given a method of examining thick crystals.

Van der Graaf irradiation has been found to leave single polythene crystals undamaged under conditions where the same material in bulk form would be markedly affected.

Curing of Polyesters

Approximately 600 g. of linear unsaturated polyester of the following composition:

Maleic anhydride	1 mole,
Adipic acid	1 mole,
Ethylene glycol	2 moles

have been prepared from purified starting materials, and freed from unreacted maleic anhydride and low-molecular-weight polyester fractions by successive extraction with boiling distilled water and benzene.

A series of 27 experiments on the curing of a commercial styrenated polyester in benzene solution to determine the effect of variables (e.g., polyester concentration, catalyst concentration and time of reaction) on the yield of cross-linked material is almost complete.

/Accelerated .....

Accelerated Aging of Plastics

Many plastics materials, including nylons, polypropylenes, polycarbonate, polyacetal, polymethylmethacrylate, styrene copolymers and various polythenes, are being subjected to accelerated aging conditions in water, and in wet and dry atmospheres at elevated temperatures.

Of the materials tested at 150°C in dry conditions the polypropylenes (dependent on stabilising treatment) and polycarbonate are still satisfactory after 16 days, but the polyacetal has less than 20 per cent of its original tensile strength after seven days and also shows considerable and progressive loss of weight with time.

Tests on various nylons, 6.6, 11 and 6.10,confirm that nylon 6.6 degrades rapidly in wet atmospheres as also do the other nylons, but surprisingly nylon 11, which absorbs much less moisture than nylon 6.6, degrades more rapidly. Commercially stabilised nylons 6.6 and 6.10 are far more resistant to degradation; under both wet and dry conditions the results agree with those of earlier work here on stabilising nylon by impregnation with diphenylamine. In the early work nylon 6.6 was treated by immersion in molten diphenylamine at 150°C. More recent work with nylons 6.6, 6 and 11 shows that the same effect can be obtained by immersing them in a solution of diphenylamine in alcohol at room temperature.

Permeability of Polymer Films to Water Vapour: E.M.R. with Imperial College

Apparatus has been constructed for the measurement of sorption and permeation over the range 30° - 70°C. Preliminary experiments and calibration are being carried out using polymethyl methacrylate, and techniques of casting films of the n-alkyl acrylates (on which the first part of the programme will concentrate) are being worked out.

Measurement of the Physical Properties of Polymers

The repeated requests by Service departments for information on the physical properties of plastics over the temperature range -60° to +60°C, are being met by measuring such properties as shear strength, tensile strength, impact strength, and coefficient of linear expansion over the specified temperature range. Data sheets will in due course be issued. The effect of storage conditions is also being determined under hot wet (60°C/100 per cent r.h.) and hot dry (60°C) conditions; a small tensile specimen is being used for the tests and testing is being carried out monthly over a 6 months period.

Materials under test initially are 2 grades of rubberised polystyrene, polypropylene and polycarbonate. Owing to the limited supply of the last mentioned material, not all the tests are being done on it.

/VI .....

VI RUBBERS

VI.1 ARMAMENTS

VI.1.1 Ammunition

Development of Butyl Rubber Composition Fully Compatible with Explosives

A compatible mix has been developed and a draft report on this work has been prepared. As occasion arises the use of this type of mix is being recommended for Service use.

The Effect of Propellants on Rubbers

Some common rubbers have been tested in contact with single- or double-base propellants for two years at 60°C. Results of tests are now being assessed. A further trial of less common rubbers, e.g., fluorinated elastomers, polyurethanes, is continuing.

Storage Life of Service Components

Rubber sleeves, to C.S. 2874, for shot G.F.17 pdr./77 mm A.P.D.S. are still in good condition after storage for six years at either Singapore or Cosham (O.B. Proc. 37, 712).

Rubber sealing rings from 20 pdr. A.P.D.S. rounds are in good condition after seven years storage at Cosham.

VI.5 ENGINEERS EQUIPMENT

VI.5.1 Fuel Tanks

Collapsible Fuel Containers

The Services require containers holding upwards of 10,000 gallons of petroleum fuels, which can be rolled up when empty to facilitate transport. They are to be used both for marine transport (towed by a tug) and for temporary static storage on land; for the latter they are expected to have a minimum life of six months, and for the former many years.

Containers have been made of nylon cloth proofed with neoprene on the outside and butadiene-acrylonitrile on the inside. When tested under constant load in air at room temperature the cloth retains only 70 per cent of its initial strength after six months but subsequent deterioration is very slow; the rubber proofing has little effect on the rate of deterioration.

A method of measuring ply adhesion by direct tension normal to the surface of the fabric has been developed; this appears superior to the stripping tests previously used. In one type of fabric the ply adhesion drops to 70 per cent of its initial strength after one week in petrol containing 18 per cent aromatics at 40°C, but subsequent deterioration of the bond strength is negligible. The intention is to investigate the influence of the weave pattern of the cloth on ply adhesion.

/In .....

In the static storage container there are only low stresses, and cemented joints are used. The behaviour of these joints has been examined thoroughly in collaboration with M.E.X.E. and the National College of Rubber Technology. Serviceable tanks are in use.

In the towed container (known as a Dracone), larger stresses are expected, and sewn joints have been recommended and so far found satisfactory. A detailed investigation of their strength and endurance is in hand.

Methods to Determine the Tensions in a Flexible Envelope Containing Liquid

Two small-scale flexible pillow tanks have been built. One was made of polythene "layflat" tube and the other of a lightweight rubber-proofed cotton fabric. The tension in the envelopes when full was determined by:

(i) strain measurement,

(ii) applying Hawthorne's relation between girth and hydrostatic head,

(iii) applying an approximate relationship which assumes any cross-sectional shape is a rectangle with semi-circular additions on each of the two shorter sides,

(iv) indentation of the envelope by a probe, the tension being calculated from values of probe load and the angle between envelope and probe at the bottom of the indentation,

(v) indentation of the envelope by a probe, the tension being calculated from values of probe load, depth of indentation, and maximum radius of indentation.

Values of tension obtained by methods (ii) to (v) were compared with the values obtained by method (i) these being assumed to be accurate determinations. The theoretical methods (ii) and (iii) were satisfactory. Method (iv) failed because no allowance was made for the additional tension due to the probe load; this could be allowed for in method (v) which proved quite successful. A report has been drafted.

VI.5.4 Brake Cylinders

The Effect of Hydraulic Brake Fluids on Rubber Components

German and British hydraulic brake components, based on natural rubber, have been tested by immersion in hydraulic brake fluids from these countries. A report has been prepared which shows that the rubber components are similar to one another in their composition and filler content, and that their low temperatures properties are indicative of natural rubber. One of the British fluids proved to be the most satisfactory; the remainder caused the rubber components to deteriorate within 100 days of immersion.

/VI.6 .....

VI.6 MATERIALS AND PROPERTIES

VI.6.1 New Polymers

Polymers Containing Phosphorus - Carbon Linkages: E.M.R. with Manchester College of Science & Technology

The possibility of the existence of $CF_3.P:CF_2$ (the phosphorus analogue of hexafluoropropylene) has been investigated, since it would be of great value in synthesis. There are good indications that it is formed by the dehydrofluorination of $CF_3.PH.CF_3$, but, because of the methods so far employed, it has not yet been isolated.

Routes to the compound $CF_3.PH.CF_3$ have been investigated in some detail and it can now be prepared in good yield by relatively simple procedures.

Internal Pressure of Polymers

Modification of the piezometer used in the measurement of the internal pressure of polymers has resulted in the elimination of vacuum voids, and has enabled a greater range of temperatures to be used. Using the modified apparatus the internal pressures of natural rubber, polyethylene and polytetrafluoroethylene have been measured. A report has been written in which these results are discussed and compared with those obtained for benzene, n-decane, squalene and carbon tetrachloride. A further report on the thermodynamical concept of internal pressure, and of the derivation of the formulae used, is in preparation.

During the physical measurements on polytetrafluoroethylene a discontinuity in the specific volume/temperature relationship became apparent, which was attributed to a crystalline transition in the polymer. A more detailed examination of this transition has enabled the extent of its effect on the value of the coefficient of thermal expansion to be ascertained.

VI.6.3 Properties

Chemistry and Physics of Rubber: E.M.R. with Research Association of British Rubber Manufacturers

(a) Dynamic Properties

Work continues on the dynamical behaviour of carbon-black-filled rubbers. At low amplitudes (0.002 - 1.0 per cent) the dynamic modulus, internal friction and resilience depend on the amplitude - the non-linearity depending on the deformation history of the specimens. A yield point exists at low strains, which depends on the concentration of carbon black.
These results show a striking similarity to the behaviour of non-Newtonian liquids on shearing and many of the same mathematical treatments can be applied. In particular, the structure changes can be interpreted in terms of the breakdown of the chains of carbon black particles.

/(b) .....

(b) Stress Relaxation

Continuous and intermittent stress-relaxation measurements have been used to distinguish between the cross-linking and chain scission reactions. Cross-linking during aging occurs with the radicals involved in the degradation process. Some work has been carried out on the effects of degree of cure and amount of carbon black on stress relaxation, but the emphasis has been on the elucidation of the degradation mechanism of butyl rubber.

Accelerated Aging of Rubbers

A polyether urethane rubber is still in good condition after being subjected to wet conditions at 40°C for 12 months.

A report on the resistance of polyurethane rubbers to petrol and moist conditions is in preparation.

The Effect of Swelling on some Physical Properties of Nitrile Rubber

By using an apparatus designed to measure elongation under stress of strips of rubber in varying environments, it has been shown that relaxation of up to 8 per cent of the original length can occur with nitrile rubber after less than 6 hours immersion in certain swelling media at room temperatures. The effect of swelling on tensile strength and elongation at break of medium acrylonitrile rubbers is being studied, and a further series of tests has commenced on neoprene and other elastomers.

VI.6.7 Irradiation of Elastomers

The Effect of High-Energy Radiation on Plastics and Rubbers

Work is in progress on the irradiation of nylon 6.6, polycarbonate, and polyacetol moulded specimens and on a comparative study of the properties of the irradiated materials.

Reports on the cross-linking of natural rubber and on the degradation of polyester urethane rubber, both by electron irradiation, have been prepared. A report has been written on the mechanism of degradation of polytetrafluoroethylene by ionising radiation.

/VII .....

VII ADHESIVES, SEALING COMPOSITIONS AND VARNISHES

VII.2 ADHESION

Adhesive Strength Measured by the Torsional Shear of Annular Joints

If an annulus is narrow compared to its mean radius, nearly uniform shear stresses are imposed by torsion. Such adhesive joints are being used to investigate the fundamentals of adhesive strength and the effect of such parameters as the thickness of the joint. Earlier work under extra mural contract failed to develop replicate joints with reproducible characteristics, without which further advance was impossible. This difficulty has now been overcome, at any rate with one adhesive, and information is being collected on the effect of variation of width, thickness, contraction during setting and so on. It is hoped that the criterion of failure of the adhesive will emerge - whether, for example, fracture takes place when a critical stress (Tresca) or strain (St. Venant) is reached.

Non-destructive Testing for Adhesion in Thin Laminates

Two laminate structures have been tested by dynamic flexure. One consists of two thin mild steel plates bonded together by a film of cold-setting Araldite, the other of two similar mild steel plates separated by a polythene film. In the former case perfect adhesion is assumed and in the second the polythene film represents an unbonded adhesive. It is hoped that adhesion and non-adhesion may be distinguished non-destructively in this way.

The two structures were loosely held in circular clamps and the centre was dynamically flexed by the impact of a steel ball suspended as a simple pendulum. The time of contact between ball and plate was measured electrically. It has been found that the time of contact for the unbonded structure is measurably longer than that for the bonded one. Theoretically (Report DMXRD/PHYS/59/1) the ratio should be 1.5 and experiments indicate a value of 1.8.

VII.3 SEALING COMPOSITIONS

Cement R.D.1286

R.D.1286, a chemically-setting cement developed in this Establishment and based on the reaction between "Cellobond H.8160", a polyphenol derived from cashew nut-shell liquid, and paraformaldehyde, is now widely used in Service (ca. 10 tons per annum). The curing of this cement has been investigated both from the point of view of the changes in physical properties and kinetically.

The mixed cement initially yields a rubber-like material of which the physical changes during polymerisation can be followed more conveniently than in ordinary rubber vulcanizates. Immediately after gelation it shows Hookean behaviour in simple extension. As further crosslinking occurs the stress/strain curves at first conform with the statistical theory of rubber elasticity; then the phenomenological (Mooney-Rivlin) theory is apparently obeyed. Finally the relation again appears Hookean. The modulus increases through the range 1 to 10^5 p.s.i.

/Cement .....

Cement R.D.1286 is probably fully cured when there is one cross-link per phenolic nucleus. Its change in tensile strength during cure conforms with the theory of F. Bueche. The tensile modulus, strain energy and elongation at break, and the density, all show inflexions corresponding to complete cure with methylene links. The solubility parameter does not vary appreciably with the degree of polymerisation; the experimental value agrees with that calculated from molar attraction constants.

The chemical kinetics of the polymerisation have been investigated by measuring gelation times and by measuring the Young's modulus of the rubbery product at intervals.

The reaction leading to gelation is first-order with respect to formaldehyde, and has an activation energy of about 20 kcal/mole. The post-gelation cure is also first-order with an activation energy of 23 kcal/mole. On prolonged heating the rubber continues to stiffen, up to a maximum modulus. This "overcure" reaction is also first-order, and very much slower at elevated temperatures than the formaldehyde crosslinking reaction. The specific reaction rates, k_1 for the curing reaction, and k_2 for the overcure reaction, are given by the following Arrhenius equations:

$$k_1 = 5 \times 10^9 \exp(-23 \times 10^3/RT)\ s^{-1}$$

$$k_2 = 2 \times 10^{-2} \exp(-8 \times 10^3/RT)\ s^{-1}$$

From the practical viewpoint, these investigations have had the important result of showing that the overcure reaction, which embrittles the cement and is therefore undesirable, is negligibly slow under temperate conditions of storage, and would only be expected to become noticeable when the cement had been continuously exposed to tropical sunlight for months.

VII.4 VARNISHES

VII.4.3 Physical Testing

Mechanical Properties of Detached Surface Coatings

Surface coatings (e.g., paints, varnishes) are stressed during exposure in various ways; for example, fluctuations in temperature and humidity impose relatively small stresses slowly, whereas mechanical shocks (impact, abrasion) impose sudden large stresses. Meanwhile chemical changes are taking place, due to sunlight in the presence of oxygen, which eventually degrade the film. When the strains due to imposed stresses exceed what the film can accommodate, it may crack (loss of cohesion), peel (loss of adhesion) or flake (loss of both adhesion and cohesion).

Tests which would predict at an early stage the ability of a film after prolonged exposure to withstand and recover from the effects of stresses would be valuable. The usual practice is to expose coatings either outdoors for long periods (2 to 4 years), or to accelerated weathering cycles the results of which cannot be considered reliable. After exposure, coatings are evaluated by simple mechanical tests, for example scratching or bending, which assess combinations of physical properties such as hardness, flexibility and adhesion, and by visual examination. None of these tests measures

/fundamental .....

fundamental properties of the film, such as the modulus, elastic limit, yield point, tensile strength and extension at break. These properties can best be measured on detached films.

Seven paints, having a range of performance from good to bad (on outdoor exposure), have been selected by members of the Joint Panel on Adhesion and Accelerated Weathering of Paints and Varnishes (a sub-committee of the J.S.M. (N-M) Advisory Board R. and D. Committee), and the mechanical properties of these surface coatings are being assessed after outdoor exposure or accelerated weathering cycles, in an attempt to correlate the two forms of trial.

Uniform films are formed on tinplate, and replicate panels exposed to natural and accelerated weathering. At intervals, panels are withdrawn, and the films are detached and tested by extension at a constant rate of straining and by measuring creep under constant load. This enables changes with time of exposure to be followed, and different exposures to be compared.

Preliminary results show that surface coatings with good performance on outdoor exposure rapidly develop and maintain high extensions at break and good elastic recovery, whilst less resistant coatings have low extensions at break and poor recovery.

It is intended in addition to study the effects on the films of irradiation by electrons and by ultra violet light, and to include a study of the adhesion of surface coatings.

/XX .....

XX SOLID ROCKET CHARGES

XX.4 INSPECTION METHODS

XX.4.1 X-ray Inspection

Fluoroscopy

The Mullard image intensifier apparatus has been evaluated using our 150 kV fine-focus rotating-anode set; a report is in preparation. The sensitivity has been found to be better than one per cent with aluminium plates and wire penetrameters; using grooved propellant slabs, one per cent sensitivity is only achieved under ideal conditions. This is inferior to conventional radiography which has about twice this sensitivity under similar conditions.

The equipment is now in regular use in E.R.D.E. as a screening method for assessing the smaller propellant charges, with consequent reduction in usage of X-ray film. Examination, by both methods, of 2-inch cubes after hot storage has confirmed that normal radiography is definitely more sensitive than the present fluoroscopic apparatus.

Radiography

Using propellant PU, conversion factors have been established between sensitivities determined with conventional aluminium wire penetrameters and propellant penetrameters; this will enable the conventional penetrameters to be used in routine propellant work.

Characteristic curves have been detailed for a series of industrial X-ray films, and contrast and resolution compared. It was concluded that Ilford Industrial C and CX and Kodak Crystallex are equally suitable for cordite charges. Exposure curves for propellant SUK and PU have been prepared; a report is in preparation.

XX.4.2 Ultrasonic Inspection

Assessment of the Mark III equipment has continued. A 3/16-inch diameter hole can just be detected in a 16-inch-thick slab of C.P.3 propellant with this equipment but 12 to 14 inches of propellant will be the maximum for routine inspection owing to electronic "hash" at the highest voltages.

New lead zirconate transducers have also been tried, in place of the normal barium titanate ones, and have given improved sensitivity. A short length of Wolfhound charge has been successfully inspected horizontally, without vibration difficulties, using the transmitting transducer in the conduit; a drilled hole 1/10 inch in diameter was detected. This technique is to be investigated for other charges which cannot be inspected satisfactorily at present, owing to their awkward geometric shapes.

/XXI .....

XXI SOLID PROPELLANTS FOR ROCKETS

XXI.1 COLLOIDAL PROPELLANTS - EXTRUDED

XXI.1.1 Improved Manufacturing Techniques: Solventless Extrusion

Snifter

To avoid assembly of charges from sheet material a small die has been machined from the solid for extruding the complicated Snifter II charges of 0.08 inch web thickness. Satisfactory charges have been extruded for test firings; a similar die for Snifter III (0.04 inch web) is being prepared.

Multitubular Charges for Power Cartridges, etc.

Difficulty has been experienced over a long period in designing satisfactory extrusion dies with rigid pins for solventless charges with 19 or more perforations, to give charges with high progressivity of burning.

A new technique has been devised in which flexible Teflon-coated Bowden cables are used as pins in a multi-hole choke plate, which gives a symmetrical feed for the propellant around the cables. This technique enables the number of perforations to be greatly increased; some 127-hole charges, three inches in diameter, with a web thickness of around 0.15 inch, have been supplied to A.R.D.E. for travelling charge gun experiments. A 108-hole extrusion was also made simply by re-arranging the Bowden cables in the same die assembly.

The joint between the Bowden cables and the nipples holding them in the choke plate is not strong enough for the reliable extrusion of harder compositions. For these, however, flexible steel wires, silver-soldered to the nipples, can be used instead of Bowden cables, the flow of the propellant bending them to the correct curve. Charges with 19 perforations, in a platonised composition F.488/1058, have been supplied to A.R.D.E. for trials as an experimental replacement for HSC in seat-ejection cartridges.

XXI.1.2 New Compositions

Problems Associated with the Development of Platonised Compositions

Lead Phthalate/Carbon Black System

The use of lead phthalate/carbon black in various combinations gives a versatile method of controlling the burning rate. This lead compound gives propellants which withstand hot storage with little change in burning rate and show notably good resistance to cracking. A composition with 4 per cent lead phthalate and 0.4 per cent carbon black having a burning rate of 0.5 inch/s is being fully assessed as a possible replacement for PU. Composition F.488/1058, burning at 0.65 inch/s, is also being examined as a possible standard. A number of composition variants, such as calorimetric level, amounts and sources of lead compound, percentage of carbon black, have been studied to decide the best factors to select for satisfactory ballistic control in production. Processing aspects, such as the amount of rolling, have been examined; limits have been proposed for the specification of F.488/1058.

/Ukarb .....

Ukarb 340 Carbon Black

This commercial carbon black was chosen some time ago as a reliable ballistic additive, but the properties of a recent consignment (lot P3/39298) differed from earlier lots. Three further samples were obtained, spread over a period of production, and have been checked in three propellant compositions as well as being examined in the laboratory. There was little difference between the various samples when used at 0.1 per cent by weight in F.488/1537. However in F.488/1046 and F.488/1058, which contain 0.8 per cent carbon black, lot P3/39298 again gave higher burning rates and higher mesa pressures than the other samples. Specific surface and diphenylguanidine adsorption tests indicated that the P3/39298 was finer than usual.

F.488/1058 was then made using amounts varying from 0.3 to 0.8 per cent of sample P3/39298. The peak burning rate ranged smoothly from 0.42 inch/s at 1000 p.s.i. to 0.76 inch/s at 1750 p.s.i. It appears that variation in the quality of Ukarb 340 can be allowed for by varying the amount used, and 0.6 per cent of this more active sample is equivalent to 0.8 per cent of the normal material.

Aluminised Platonised Propellants

In some platonised C.D.B. compositions the addition of about 5 per cent of aluminium has suppressed resonance and also increased S.I. An increase in S.I. from the extruded F.488/807 type composition would be very advantageous and will be assessed in an experimental Gosling motor; small batches have been made of this composition, with 3, 6 or 9 per cent of added atomised aluminium. The plateau was practically lost with 3 per cent and disappeared completely with 6 and 9 per cent aluminium. The effects of varying proportions of "lead stannate" and aluminium are being examined.

The Suppression of Flash from Gosling V.A

It was found that replacement of one-fifth of the Gosling charge by a composition containing 20 per cent potassium hydrogen tartrate (F.499/7, JU) eliminated flashing and also the so-called "g" pulse which had caused Seaslug flight trial failures. A specification has been drafted for propellant JU (F.499/7) and sent to D.G.W. (N.O.I.D.) for completion.

Meantime, R.N.P.F. has reported difficulty with the quality of Gosling extrusions of JU. Little difference has been found here in processing characteristics between JU and similar compositions heavily filled with potassium cryolite or sulphate. It was thought advisable to confirm this, and factory scale manufacture of Gosling extrusions has been arranged at R.N.P.F., with the potassium cryolite variant (F.499/13).

There is little basic information on this use of sections of flashless increments with platonised propellants. To determine whether small motors can give useful indications, two flash trials have been carried out at Waltham Abbey on 3-inch tubular charges fired statically under standard conditions. In the first trial, the replacement of either 15 per cent or 25 per cent of the PU charge by F.499/7 (potassium hydrogen tartrate), F.499/13 (potassium cryolite), or F.499/17 (potassium sulphate) suppressed the flash. In the second trial, only 10 per cent of the PU was replaced, so that the potassium compound was reduced to 2 per cent of the whole rocket charge. There were occasional flashes towards the end of burning, apparently due to interference and re-ignition at an adjacent surface.

/With .....

With 5 per cent only of flashless increment, all charges gave appreciable re-ignition. All three potassium compounds were about equally efficient in eliminating secondary combustion, in line with previous work on gun flash, although potassium hydrogen tartrate contains only half as much potassium as potassium cryolite or sulphate.

The Gosling VA has a lower expansion ratio and a longer burning time than the rockets fired at E.R.D.E., but this would hardly be expected to necessitate doubling the amount of chain-breaking catalyst in the gases. This subject has been discussed with R.P.E., who are arranging further trials with the 5-inch C.D.29 charges.

XXI.1.3 Physical and Mechanical Properties

Cracking on Hot Storage

Lengths of PU Gosling charges have shown no cracks after 26 months at 120°F (49°C) and even a 6-inch solid PU charge took 15 months to crack at 120°F. However, the occasional cracking of Gosling charges on O.B. storage trials at R.P.E. Westcott, after only 3 to 4 months at 120°F, has forced the conclusion that there is a very wide spread between lots. It must therefore be assumed that the critical temperature of the Gosling charge is 110°F (43°C) rather than 120°F, and further O.B. trials will check this.

Experiments with 4.3-inch diameter PU charges have shown that manufacturing flaws, which were detectable by X-ray examination before hot storage, did not promote early cracking. These results confirmed similar experiments with SUK charges, where only one case indicated that a flaw slightly accelerated cracking.

The flashless propellant for use in the venturi end of the Gosling motor, JU, with 20 per cent potassium hydrogen tartrate, has given a spread of cracking times generally equal to or higher than PU in tests of 2½-inch cubes at 140°F(60°C). It appears that this is about the upper critical size at this temperature; 90 per cent residual stabiliser was found after 3 months at 140°F and 78 per cent after 6 months. Cords of F.499/13, an alternative flashless propellant containing 20 per cent potassium cryolite, gave similar cracking results to PU when tested as solid cords at 140°F.

Supply of Propellant to Users

Quantities of experimental extruded propellant have been provided as follows:

(a) Inhibited charges of propellant F.488/1079 to Fairey Engineering for use as power sources in Project 12 test firings.

(b) Rocket charges to Martin Baker Co., for preliminary experiments on a rocket-assisted pilot ejection seat. A tubular charge in F.488/807 has been supplied initially, but cruciform and cog charges in the same propellant are being made to give a range of thrusts and operating times between 0.6 and 0.2 second. Quantities of a multi-hole platonised propellant are also being supplied to improve the performance of the primary cartridge.

(c) Sheet propellant (F.488/807) has been sent to R.P.E. and to R.O.F. Chorley for assembly as Snifter charges.

/(d)

(d) Several compositions, giving a range of gas composition and temperature, are being supplied to A.R.D.E., Langhurst for experiments to give an increased output to the infra-red tracking flare for the Sea-Cat target-drone.

Routine Tensile Testing of Cordite Cords

A Tensile Test Manual has been prepared and issued covering the operation of the routine tensile test. Testing and conditioning procedures have been improved, modified, and brought into line at the various factories and inspectorates concerned. New methods of lining the wedges and setting the zero have been brought into use.

The testing of ¼-inch diameter cords has been studied. So far, no completely satisfactory design of grip has been found; a new type of grip is being developed by Tensometer Ltd.

XXI.2 COLLOIDAL PROPELLANTS - CAST

XXI.2.1 Manufacturing Techniques

Aluminised Casting Powders

Separate Extrusion and Cutting Process

The technique for producing experimental batches of up to 300 lb is thoroughly established, using acetone/alcohol as solvent. About forty batches have been manufactured in this period, mainly variants on F.452/284 (pyro N.C. 31.3, N.G. 10.0, ammonium perchlorate 34.8, aluminium 23.1, 2-N.D.P.A. 1.0) involving:

(i) Alternative possible stabilisers, such as carbamite, magnesium stearate, resorcinol, litharge,

(ii) Replacement of N.G. by D.E.G.N.,

(iii) Partial or complete replacement of ammonium perchlorate by picrite.

Densities have consistently exceeded 97 per cent of theory and bulk densities have exceeded 1250 g/l.

Two 300 lb batches have been sent to I.C.I. Summerfield.

Press Cutter

A satisfactory procedure has not yet been devised for press-cutting high-impulse casting powders, which are too sticky and agglomerate when made with acetone/alcohol, and low in density when made with the usual ether/alcohol solvent. A large number of small-scale manufactures of F.452/284 have been carried out with different solvents and incorporating procedures, to obtain powders of a satisfactory density made from non-sticky doughs of the ether/alcohol type. Laboratory work indicated that the addition of up to 10 per cent of water to the ether/alcohol solvent mixture reduced the viscosity of nitrocellulose suspensions. A satisfactory density (97 per cent theoretical) was obtained on the small scale with a mixed solvent, ether/alcohol/water 54/36/10, but was not repeatable in the larger scale 60 lb

/incorporators .....

incorporators.

Further attention has been given to the possibility of press-cutting the "sticky" doughs which result from the use of acetone-type solvents. A 60 lb manufacture of F.452/271 with acetone only as solvent was press-cut on the 250-ton Finney press and the granules handled appreciably better than is usual when the solvent is acetone/alcohol. Promising techniques include faster cutter speeds and fluidisation of the solvent-wet casting powders by the use of an "air slide" to prevent agglomeration.

Considerable quantities of more conventional compositions have been made using the press cutter with the Finney 250-ton press. Casting powders containing high proportions of only aluminium (up to 36 per cent) or only ammonium perchlorate (45 per cent) have been press-cut satisfactorily in 150 lb batches.

Miscellaneous Casting Powders

1700 lb of ATN, 2500 lb of D.B.I.(D1) and 120 lb of C.C.V. were supplied early in the period to I.C.I. Summerfield to maintain motor development, there being temporary difficulties at Ardeer. These successful manufactures provide further evidence of the reliability and value of the press cutter and, in the case of ATN, of its applicability to the low-level, 8-inch, gun propellant presses in the R.O.F.s. I.C.I.(Ardeer) is considering using the press-cutting device in their new experimental plant and also to give improved quality commercial shot-gun propellants.

Manufacture of Case-Bonded Aluminised Propellant Rockets

Following the success of the 2-inch double cone and cylinder (K) motor for ballistic assessment work, small numbers of 5-inch motors have been made with propellant thickness of 1¼ inches (J motors) and ½ inch (L motors) for special S.I. investigations.

Multiple-casting stands are used for these motors in association with the standard 6-inch casting plant.

XXI.2.2 Ballistic and Mechanical Properties

Propellants Containing Aluminium and Ammonium Perchlorate

Stability

A screening test has been established to avoid damage to the conventional stability testing equipment by unstable formulations; ½-inch cubes are heated in an isolated oven at 95°C to self-ignition. Figures ranging from 20 to over 300 hours have been obtained and compositions have been selected for standard stability tests. The screening test indicated that magnesium stearate and zinc oxide additions give marginal improvements in stability, whilst the use of carbamite or N.M.A. in place of 2-N.D.P.A. offers little advantage. No improvement in stability resulted from the use of 1 to 2 per cent of calcium carbonate, O-aminophenol or propyl gallate. Marked improvement resulted from the use of up to 1.4 per cent resorcinol. Attempts to obtain indications of chemical stability from the pH of the water extract of these propellants or their ingredients were not successful.

/Gas .....

Gas Permeability

The permeability to nitrogen of compositions containing 23 per cent pyro N.C., 35 per cent plasticiser and 42 per cent filler is higher than that of conventional propellants, and there is little change when ammonium perchlorate is replaced by picrite or when atomised aluminium is used in place of flake aluminium. Between 30° and 60°C the permeability is about twice that of SUK (48.4 per cent nitrocellulose), which is twice as permeable as C.P.3 (61 per cent nitrocellulose). The permeability appears to depend mainly on the N.C./plasticiser ratio. Hence, the abnormally short cracking lives of the original "high impulse" C.D.B. compositions must be ascribed mainly to unusually high rates of gas formation.

Aluminised C.D.B. Propellant

More than four hundred 2-inch case-bonded K-rounds have now been successfully fired, including a few rounds at -60°F (-51°C) and others cycled to -60°F (see below).

Measured S.I.s of around 243 lb.s/lb have been obtained in K-rounds with the following types of composition, which are discussed in detail below.

(i) N.G. compositions containing aluminium and ammonium perchlorate,

(ii) D.E.G.N. compositions containing aluminium and ammonium perchlorate,

(iii) N.G. compositions with part of the ammonium perchlorate replaced by nitroguanidine.

Compositions giving slightly lower S.I.s, below 240 lb.s/lb in K-rounds, are:

(iv) N.G. compositions with added aluminium only.

N.G. Compositions with Aluminium and Ammonium Perchlorate

Compositions have been formulated at filler contents of 20 and 42 per cent with wide variations, such as aluminium 1.4 to 16.8 per cent and ammonium perchlorate 4.9 to 25.5 per cent, without effect on measured S.I. Consideration of density requires the aluminium content to be as high as possible and a propellant with aluminium 16.8 and ammonium perchlorate 25.5 per cent (F.452/284/19) has been standardised to test minor variations. No effect on S.I. was obtained by replacing pyro N.C. by guncotton or by the use of up to 1.4 per cent resorcinol in the final propellant.

After early difficulties, propellants containing both aluminium and ammonium perchlorate can now be obtained with fair chemical and cracking stabilities, by the addition of 1.4 per cent resorcinol. Chemical stabilities similar to cordite Mk.I and cracking lives at 80°C of between 5 and 10 days are obtained (F.452/302/19); this variability is excessive, but it is thought to be linked to water content and is being investigated.

The burning rates of this type of composition are high and range from 0.65 to 1.05 inch/s at 1000 p.s.i. depending upon aluminium/ammonium perchlorate proportions. Burning rates are reduced slightly by the presence of 1.4 per cent resorcinol and an improved temperature coefficient πk of 0.20 per cent per degree F is obtained, compared with 0.28 per cent/deg.F for the unmodified composition. The pressure exponent is also reduced from about 0.53 to about 0.40 by the use of resorcinol.

/D.E.G.N. .....

D.E.G.N. Compositions

These were originally formulated to obtain improved mechanical properties and greater stability than with N.G. Only two aluminium/ammonium perchlorate ratios were tested and S.I.s were similar to the N.G. counterparts.

Substituting D.E.G.N. for N.G. gave chemical stabilities up to twice that of cordite Mk.I. Cracking lives are improved to 16 days. The addition of resorcinol further improves cracking lives at 80°C.

A burning rate of 0.8 inch/s at 1000 p.s.i. with a typical formulation is some 0.15 inch/s lower than that of the N.G. counterpart. The temperature coefficient πk of 0.21 per cent/deg.F for a D.E.G.N.-resorcinol composition is similar to the corresponding N.G. compositions.

The available results show that D.E.G.N. compositions with 1.4 per cent added resorcinol are generally superior to the N.G. counterpart in mechanical properties at lower temperatures, chemical stability and resistance to cracking and they are thought to be suitable for development for large motors with a life of 5 to 7 years at 90°F (32°C).

N.G./Picrite/Ammonium Perchlorate Compositions

In view of the good stability shown by picrite gun propellants, compositions have been made in which part of the ammonium perchlorate has been successively replaced by picrite.

High S.I.s are given by compositions with up to 12 per cent of picrite (F.452/336/19) and a similar ammonium perchlorate content. Burning rates down to about 0.65 inch/s at 1000 p.s.i. are achieved, with a low pressure exponent of about 0.40 when resorcinol is also present.

Chemical stabilities are improved on replacement of ammonium perchlorate by picrite, to give up to three times the life of cordite Mk.I. Picrite does not increase cracking life and resorcinol also is necessary to obtain lives of about 10 days at 80°C; this type of composition may be used where a high degree of chemical stability is required, but it has not yet been completely assessed.

Aluminised N.G. Compositions

Measured S.I.s in K-rounds approaching 240 lb.s/lb can be obtained by the use of up to 15 per cent of aluminium in very hot double-base matrices. Larger proportions of aluminium lead to difficulties in ignition and in burning at low pressures. Burning rates of this type of composition are of the order of 0.5 to 0.6 inch/s at 1000 p.s.i. but with a high pressure exponent of 0.7. These formulations with aluminium alone have good chemical stabilities (about twice that of cordite Mk.I) but only moderate cracking lives; the addition of resorcinol is being tried.

Compositions Suitable for Further Development

Further work is necessary to develop more fully the slower burning compositions containing picrite and ammonium perchlorate (e.g. F.452/336/19) and those containing aluminium alone (e.g. F.452/360/19) which may have uses where exceptional stability is required. A more complete small-scale assessment has been made in K-round motors of two representative high impulse N.G. and D.E.G.N. compositions, F.452/302/19 and F.452/368/D1. In addition to ballistic assessment for S.I., burning rates, and temperature

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coefficients (between +120° and -20°F, 49° and -29°C) temperature cycling and storage trials are in progress.

Twelve K-round motors of each composition have successfully withstood ten cycles at three temperature cycling tests of progressively increasing severity.

Test A: -20°F for 16 hours, ambient for 8 hours, +120°F for 16 hours, ambient for 8 hours.

Test B: -40°F (-40°C) for 16 hours, ambient for 8 hours, +120°F for 16 hours, ambient for 8 hours.

Test C: -60°F (-51°C) for 16 hours, ambient for 8 hours, +120°F for 16 hours, ambient for 8 hours

No changes were apparent at visual and X-ray inspection after cycling; the motors behaved normally when fired at ambient temperature.

The tests with this simple motor design were not severe enough to distinguish between the merits of N.G. and D.E.G.N. compositions at low temperature. It would be expected that the higher elongation of the D.E.G.N. composition at low temperatures would allow a larger and more complex charge to be cycled to a temperature some 20°C lower than the N.G. composition.

Other trials with these compositions gave no ignition difficulties down to -60°F (-51°C) and charges burned quite regularly with little or no change in S.I. from ambient values. Both propellants ignite normally and burn satisfactorily down to 300 p.s.i. Measured uncorrected S.I.s remain above 200 lb.s/lb at these low pressures and burning efficiencies appear to be little changed.

The K-round storage trial at +120°F (+49°C) is proceeding; an N.G./resorcinol composition has withstood 4 months and the D.E.G.N. composition 2 months; no deterioration has occurred.

Dense Propellant

For certain volume-limited rocket applications a net gain in total impulse might be achieved by an increase in propellant density notwithstanding a fall in specific impulse.

A composition (F.452/375/19) containing 60 per cent of litharge, with a density of 3.0 g/ml was cast in K-rounds and fired. The measured S.I. was 127 lb.s/lb at about 850 p.s.i. The theoretical S.I. calculated on the basis of forming monatomic lead vapour is 160 lb.s/lb. Globules of lead were found after firing inside the motor tube, in the venturi approach and outside the motor. The burning was less efficient than had been estimated, but litharge appears to have contributed appreciably to the S.I; a further composition with less litharge will be made.

Case Bonding

Laboratory Assessment

An aluminised D.E.G.N. propellant has been bonded successfully to mild steel, using cross-linked Formvar as bonding film; the optimum solution concentration was 10 per cent Formvar. This is an important development since the case bonding methods used by Allegany Ballistics Laboratory have

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not been successful here with D.E.G.N. compositions.

Satisfactory adhesion was obtained between epoxy-resin glass-fibre laminates and propellant; the laminates had been treated with a series of very thin coatings with decreasing proportions of epoxy resin and increasing proportions of Formvar. No bond failure occurred after 12 cycles between 120° and $-4^\circ F$ ($+49^\circ$ and $-20^\circ C$) of a tubular charge of modified ATN propellant which had been cast inside a treated 6-inch diameter epoxy-resin fibre-glass laminate tube. Soft ends to the charge were avoided by casting a 1-inch thickness of dummy propellant between perforated plates at each end; the dummy propellant was separated from the charge without difficulty.

Heat Insulators

Procedures have been devised with test pieces to obtain satisfactory bonding to both propellant and mild steel of insulating materials,ranging in properties from hard and brittle to rubbery. The following successful laboratory procedures are being assessed in K-round motors:

(i) Precoating of the metal with a stoved Redux 120 coating followed by an insulating layer of silica-filled epoxide resin EP.201, which occurs at room temperature, and a final cross-linked Formvar lacquering to bond to the propellant.

(ii) Sticking a layer of sulphuric-acid-treated Hypalon (representing rubbery material) under pressure to the motor wall by Redux 120, containing cyclohexanone, and coating with a film of cross-linked Formvar to which the propellant bonds during casting.

Temperature Cycling and Firing Trials: 5-inch Coulport Motors

This motor, which is being used to test case-bonding of C.D.B., has heavy iron end-rings designed originally to act as a "heat sink" for very hot plastic propellant. First experiments showed that ATN propellant tended to ignite at the surface which was bonded to the venturi end-ring. For the next trial, these end-rings were faced with Durestos conical washers, machined from a thick-walled tube.

After satisfactory control firings, four rounds were subjected to twelve two-day temperature cycles between 140° and $-4^\circ F$ ($+60^\circ$ and $-20^\circ C$). One of the cycled rounds fired at $-4^\circ F$ gave a sporadic high pressure and ejection of the carbon choke near the beginning of burning. Further examination of the fired cycled motors indicated that some degree of failure of the bond between the machined Durestos and propellant had occurred during firing. This failure shows that machined Durestos is not suitable for use with Formvar adhesive; alternative heat insulating materials are being examined.

Aluminised compositions F.452/294/19 and F.452/368/D2 were then fired in shortened Coulport motors using the original bare metal end-rings,. without any sign of overheating. It is thought that the difference between ATN and the aluminised propellants may be due to increased thermal conductivity of the latter.

Brittle Point Determinations

The brittle points, under rapid stress conditions, of a number of propellants have been determined by a simple test in which a bar of propellant

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0.2 inch thick and 1.56 inches long is pushed through a gap 1.50 inches wide in a time of 0.002 second. The brittle point is arbitrarily defined as the lowest temperature at which this can be done without fracture; the effective strain is about 6 per cent. When similar tests are carried out on the Tensometer, at a speed 6000 times slower, the brittle points are about 15°C lower. Measured values of the high-speed brittle points include:

TABLE 1

C.D.B. Propellant	Brittle Point, °C
TH86	-3
ARP	-4
BDI	-5
ATN	-7
TH86	-20
CCV	-23

The low brittle point of TH86 is due to the replacement of N.G. by D.E.G.N. The CCV has a very low nitrocellulose/plasticiser ratio.

High Temperature Tensile Properties of High-Energy C.D.B. Propellants

A series of constant-load tensile tests has been carried out on two high-energy C.D.B. compositions at 20°, 40° and 50°C, over a range of stresses. The propellants chosen were of the soft case-bondable type, for which it is important to ensure that too much flow does not occur at the upper temperature limit. Particular attention was given to the longer breaking times, and to the flow under stresses too small to cause fracture. Some of the results are summarised in Table 2.

TABLE 2

Propellant	CCV			T.H86		
Temperature, °C	20°	40°	50°	20°	40°	50°
Long-time strength, p.s.i.	24	14	7	74	60	
U.T.S. from routine test results at 1 inch/(inch/min)	130	50	30	230	120	90
Breaking strength at 10 s., p.s.i.	200	72	44		150	100
Long-time elongation, per cent	40	50	55	20	30	30
Long-time modulus, p.s.i.	55	22	13	520	240	170

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XXI.3 PLASTIC PROPELLANTS

XXI.3.1 Improvements in Manufacturing Methods and Filling

Production for R.P.E. Westcott

During the period under review, production of propellant for R.P.E. Westcott has been maintained at a high level, the weekly average being just over ¾ ton. The main demand has been for a propellant for the various types of Raven and for Gosling IV acceptance trials.

A specification has been written for R.D.2410, the Gosling IV propellant, which is now being manufactured at R.O.F., Bridgwater. An investigation into burning rate differences between E.R.D.E. and R.P.E. for certain lots of this propellant has shown that care in determination and comparison burnings with a standard lot of propellant will be necessary to maintain strict control of the propellant ballistics.

Variations in ballistics of lots of R.D.2406 made at R.O.F., Bridgwater have been noticed at R.P.E. and investigation of these has shown that they are due to variable amounts of breakdown of the un-milled perchlorate. The burning rate v. pressure curve changes from a straight line to "plateau" and then to "mesa" as the particle size of the perchlorate increases. This is due to increases in the burning rate at 1000 p.s.i. Changes in manufacturing procedure have been suggested to R.O.F., Bridgwater to enable them to obtain the correct ballistics.

Compositions have been developed for the following requirements:-

Guillemot Burning rate of 0.95 inch/s at 1000 p.s.i. with a pressure exponent of 0.5.

Rook Burning rate of 0.56 inch/s at 1000 p.s.i. with an increased yield value to prevent propellant flow during firing. The binder content of the propellant S.1002 has been reduced to 10 per cent to give a stiffer mix.

36-inch Motor Burning rate of 0.14 inch/s at 500 p.s.i. and with suitable rheological properties for resistance to slump under gravitational stress. The composition E.3668 has been developed for this requirement. The binder content has been reduced to 10 per cent from the normal 11 per cent and this has doubled the yield value. The composition has also been tested in the three-foot diameter slump test vessel. This is filled with propellant, giving an annulus of propellant 2 ft deep, external radius 18 inches internal radius 4 inches. This is stored with its axis vertical, and with no support on either end of the annulus. The slumping at edge of the central hole after 30 days storage was less than one inch.

Motor Filling for A.R.D.E.

During this period, 750 2-inch air-to-air rockets have been filled with R.D.2404 for trials at Fort Halstead. A further 100 2.75-inch G.A.R. motors have also been filled for ultimate despatch to A.R.D.E.

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Development of New Processing Machinery

A 50-gallon, heavy-duty, Baker Perkins incorporator has been brought into use during the last six months. Using the sigma blades originally fitted several batches of all types of propellant have been made. These batches were incorporated for half to three-quarters of an hour and the resultant propellant had good rheological properties. The batch size for this incorporator is 150 kg; the machine thus gives a four to six-fold increase in production rate.

A satisfactory method of metering polyisobutene for feeding into the Ko-Kneader has been developed. A triple screw pump is used and this develops enough pressure to feed the material into the barrel of the Ko-Kneader. The pump will deliver polyisobutene within an accuracy of 1 per cent over long periods of time. Using the constant-weigh feeder for feeding premixed solids, several satisfactory runs with inert propellant have been made.

XXI.3.2 New Compositions

Aluminised Plastic Propellants

A series of these compositions has been made to enable the effect of aluminium concentration on ballistics to be determined, at ammonium picrate levels of 0, 10, 20 and 30 per cent. The results were obtained from the strand burner and K-round firings at ambient, at high and at low temperatures.

The results of main interest are the specific impulses measured in the 2-inch K-round and the aluminium concentration at which the maximum performance is obtained. The maximum specific impulse measured was 247 lb.s/lb for a composition containing no ammonium picrate and 14 per cent of aluminium. The maxima for the 10, 20 and 30 per cent picrate levels were respectively 238, 231 and 219 lb.s/lb at aluminium contents of 15, 12 and 8 per cent. These results cover a burning rate range of 0.63 - 0.21 inch/s. at 1000 p.s.i. It should be possible to obtain the ballistics of any composition in this range by interpolation of the curves already obtained.

The pressure exponents of all compositions are in the range 0.5 - 0.6 and decrease slightly with increasing aluminium content. The temperature coefficients of pressure and burning rate at constant restriction ratio are in the range 0.15 - 0.2 per cent/deg.F. The rheological results for all propellants are satisfactory.

Extensions to this basic scheme have been made. The effect of burning rate on the measured performance at constant composition has been studied; the burning rates of the compositions have been increased by decreasing the particle size of the ammonium perchlorate and by the addition of 1 per cent of copper chromate. In this way the burning rate was increased from 0.63 to 1.5 inch/s at 1000 p.s.i. for the 14 per cent aluminium composition and from 0.58 to 1.45 inch/s for the composition containing 25 per cent of aluminium. The specific impulse increased from 249 to 252.5 lb.s/lb as the burning rate of the 14 per cent aluminium composition increased and from 234 to 242 for the 25 per cent aluminium composition. This increase associated with the higher burning rates may be due to reduced heat losses from the round or more efficient combustion of the aluminium.

Another possible variable is the particle size of the aluminium. Various grades of aluminium powder are available and propellants were made

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with powders varying in specific surface from 3,000 to 30,000 cm^2/cm^3. The measured specific impulses for these compositions showed no consistent variation of performance with particle size of the aluminium, although the pressure exponent and temperature coefficients varied considerably. The finer grades of aluminium gave valuable reductions in these parameters.

Plastic Propellant Containing RDX

Work has continued on these compositions, using a premix of RDX, P.I.B. and S.101 manufactured at R.O.F., Bridgwater. A series of propellants, containing RDX alone and RDX in combination with other ingredients, has been made. Preliminary work had shown that the following compounds - nitroguanidine, diphenyl glycol uril and 1,3-dinitro-1,3-diazacyclopentane - may reduce the pressure exponent of these propellants to a reasonable value.

All these compositions could be made easily, using the premix, although some containing finely divided organic substances hardened after mixing and could not be filled into K-rounds. The burning rates and pressure exponents of the compositions were measured both in the strand burner bomb and under rocket conditions in the K-round.

In general, the results have shown that low pressure exponents can be easily obtained below 1000 p.s.i., e.g., addition of 15 per cent of nitroguanidine gives an exponent of 0.44 below 1000 p.s.i., with a burning rate of 0.106 inch/s at 1000 p.s.i. However above 1000 p.s.i. the pressure exponent remains high; this is shown by the fact that K-round chokes are blown out by progressive burning, in most cases at pressures greater than 1300 p.s.i. One composition, containing 15 per cent of diphenyl glycol uril, gave a pressure exponent of 0.34 at a burning rate of 0.075 inch/s at 1000 p.s.i. and fired satisfactorily up to 1700 p.s.i. This additive is being investigated further.

The results show promise of giving usable compositions with low pressure exponents, low burning rates and high calculated performance and without increased sensitiveness.

Alternative Binders for Plastic Propellant

Lutanol J60 - polyvinyl isobutyl ether - has been investigated as a possible binder. It is a viscoelastic polymer very similar in appearance to polyisobutene. Compositions with it have good rheological properties and low burning rates and pressure exponents, e.g., with 40 per cent of ammonium picrate, the burning rate is 0.21 inch/s at 1000 p.s.i. and the exponent is 0.46, compared with 0.25 inch/s and 0.65 for a conventional plastic propellant. A draw-back to the use of this polymer is the relatively high brittle point of -20°C, compared with -50°C for polyisobutene. Mixtures of polyisobutene and Lutanol show little improvement.

XXI.4 POLYURETHANE PROPELLANTS

Correlation of Modified Polyester Structure with Propellant Physical Properties

The relative merits of trimethylol propane and penta-erythritol as crosslinkers in modified polydiethylene adipates have been assessed in Composition U.226 (61.5 ammonium perchlorate, 15 aluminium, 22.5 rubber, 1 Ionol). Five modified esters have been investigated: in each case the molar ratio of adipic acid to diethylene glycol was constant at 13.0:14.5.

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The molar ratios of trimethylol propane were 0.5, 0.67, 1.0, and of penta-erythritol, 0.375 and 0.50. All propellants contained one equivalent of tolylene di-isocyanate (T.D.I.)

Tensile testing at 2 inches/(inch/min) on samples cured 3 days at 60°C indicated only slight differences between the modifiers; the 0.5 molar trimethylol propane and the 0.375 molar penta-erythritol modified polyesters were slightly superior and gave propellants with elongations of approximately 14, 20, 10 per cent at +60°, +25°, -40°C, respectively. The penta-erythritol crosslinked propellant was markedly stronger at +60°C.

Generally the physical properties were improved by curing at a lower temperature; comparisons were made of samples cured at +40°, +60°, and +100°C; the cure time was increased to about 8 days at the lowest temperature.

Mix fluidities of the propellants made with the polyesters containing the lower proportions of crosslinker were satisfactory and indicated a "pot life" of between two and three hours after the addition of the tolylene di-isocyanate.

Selection of Modified Polyester for Pilot Scale Production

Because of the work reported above, it was decided to make 2000 lb of the polyester modified with 0.5 molar trimethylol propane and to use it for general development work in place of the I.C.I. Daltorol polyester. The new polyester was designated L.45.

L.45 has been satisfactory in propellants not plasticised with T.E.G.D.N; in the presence of this plasticiser, however, it has proved almost impossible to produce bubble-free cured propellant. The reason for this is considered to be the relatively slow cure reaction of L.45 (compared with Daltorol) which allows an appreciable amount of the residual water in the system to react with the tolylene di-isocyanate and produce carbon dioxide. Particular care has been taken to dry the T.E.G.D.N. to a water content below 0.01 per cent and the polyester to less than 0.02 per cent, but it has been calculated that a water content of 0.01 per cent (in the mix) could produce 55 ml carbon dioxide in every pound of propellant if the tolylene di-isocyanate is not "fixed" by reacting with the polyester. Ballistic assessment of T.E.G.D.N. plasticised propellants has continued, therefore, with Daltorol polyester; penta-erythritol modified polyesters are being examined for use with plasticiser, as in general they have shorter cure times than those modified with trimethylol propane.

Physical Properties of T.E.G.D.N. Plasticised Compositions

Tensile testing on the Hounsfield Tensometer at a crosshead rate of 2 inches/(inch/minute) has been carried out at -40°, +25° and +60°C, to determine the effect of total solids loading in the range 75 to 80 per cent, with a binder system 25 per cent plasticised with T.E.G.D.N. The effect of plasticiser content in the range 10 to 30 per cent of the total binder was studied at 77.5 per cent loading (total solids). All compositions contained 10 per cent aluminium and the remainder of the solids was ammonium perchlorate; the polyurethane rubber consisted of Daltorol polyester reacted with one equivalent of tolylene di-isocyanate.

The presence of the T.E.G.D.N. plasticiser caused a marked improvement in elongation (up to 22 per cent) and a reduction in modulus at -40°C. At ambient and above the properties were slightly inferior to those of the non-plasticised compositions. Total solids loading in the range 75 to 82 per

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cent had little effect on tensile properties of propellants containing a 25 per cent plasticised binder.

Current investigations indicate that the high-temperature physical properties of plasticised compositions can be improved by the use of different modified polyester rubbers.

Ballistics of Aluminium/T.E.G.D.N. Polyurethane Propellants

The presence of either aluminium, or T.E.G.D.N. plasticiser (usually about 25 per cent of the total binder), in polyester polyurethane propellants caused an increase in burning rate from about 0.23 to 0.30 inch/s at 1000 p.s.i; with both materials present the effect was additive and burning rates of the order of 0.42 inch/s resulted.

The rate was also affected by the binder level; the lowest level studied, 18 per cent, of which one quarter was T.E.G.D.N., gave a burning rate of 0.45 inch/s at 1000 p.s.i. when 10 per cent aluminium was present.

Low burning rates were not achieved with both aluminium and T.E.G.D.N. present; even when two per cent calcium carbonate was added the rate was reduced only to 0.33 inch/s at 1000 p.s.i.

With all the above propellants the measured (K-round) performance was in the range 228 to 236 lb.s/lb, the performance improving as the binder level decreased and the burning rate increased. For any series of compositions of increasing aluminium content the measured performance was a maximum at relatively low (5 to 10 per cent) aluminium levels. Temperature coefficients of burning rate at constant restriction ratio were low and in the range 0.10 to 0.15 per cent per deg. F.

Lower burning rates down to 0.24 inch/s at 1000 p.s.i. were achieved with aluminised, but non-plasticised, propellants, with measured performance about 228 lb.s/lb.

The combustion efficiency (measured performance divided by calculated) of all aluminised polyurethane propellants, with or without T.E.G.D.N. plasticiser, was only about 91 per cent compared with almost 95 per cent for plastic propellants.

Finely divided silica (Silon S from Messrs B.F. Goodrich of U.S.A.) was the only effective burning rate catalyst investigated; one per cent increased the rate of a T.E.G.D.N. plasticised and aluminised composition from 0.42 to 0.67 inch/s at 1000 p.s.i.

Slow-burning Polyurethane Propellants

Several methods of reducing burning rate have been investigated:

(i) Ammonium nitrate.

Substitution of some perchlorate by nitrate reduced the burning rate but increased the mix viscosity considerably. It was considered that this method of rate reduction was impractical.

(ii) Use of trichloroethyl phosphate as a plasticiser.

This ester is commonly used as a fire retardant in polyurethane

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foams; it is quite compatible with Daltorol rubber. Little reduction was obtained in burning rate.

(iii) Use of binders other than the polyester type (as typified by poly-diethylene adipate):

(a) Polypropylene glycol/hexanetriol.

This system has an intrinsically lower burning rate than that of the polyester one. For the propellant composition containing 75 per cent oxidiser and 25 per cent binder, the glycol system burnt at 0.15 inch/s at 1000 p.s.i. compared with 0.20 inch/s for the Daltorol type.

(b) Castor oil.

Castor oil crosslinked with 0.7 equivalent T.D.I. and 75 per cent loaded with perchlorate (i.e., comparable with the above composition containing polypropylene glycol) also burned at the same rate though its pressure dependence was 0.4 against 0.1. At 80 per cent loading the burning rate was 0.23 inch/s which was the same as with Daltorol; however, the presence of aluminium in the castor oil bound propellant caused a slight decrease in rate (15 per cent reduced the rate to 0.20 inch/s) compared with the increase in the case of Daltorol (15 per cent aluminium increased rate to 0.30 inch/s).

(iv) Burning rate depressants.

The use of calcium carbonate has been described previously. Lithium fluoride has also been found effective, 2 per cent reducing the burning rate of a 75 per cent loaded castor oil propellant to 0.115 inch/s.

Carbon Dioxide Evolution from Polyester/Isocyanate Mixtures

All polyesters used at present in the manufacture of polyurethane propellants contain a small proportion of carboxyl end-groups; these can react with an isocyanate to give carbon dioxide. It is important to know whether the evolution of this gas occurs mainly during mixing or on curing, and, if the latter, whether any physical defects in the propellant are likely to result.

It has been found that the rate of carbon dioxide evolution from unstirred equimolar mixtures of Suprasec SF (65/35 2,4/2,6-tolylene di-isocyanate) and dried polydiethylene adipate, held under near-vacuum conditions at temperatures of 60° and $100^{\circ}C$, is extremely slow. Using a polyester with an acid number of 2.5 mg KOH/g only 8 per cent of the total possible amount of carbon dioxide was given off after 20 hours at $60^{\circ}C$, and at $100^{\circ}C$ 19 per cent was evolved after the same time. When the acid number was increased to 16.5 mg KOH/g only 17 per cent of the theoretical amount of gas was collected after 20 hours at $60^{\circ}C$ and 45 per cent after a further 80 hours heating. The presence of ammonium perchlorate did not affect the rate. Bubbles were formed in these mixtures only when the polyester of high acid number was used or when ammonium perchlorate was present.

Subsequent measurements of the loss of carbon dioxide from unstirred solutions containing 0.3 - 0.7 ml s.t.p. of gas per gram of polyester have shown that this occurs without bubble formation and at a rate similar to that obtained with a mixture of Suprasec SF and polydiethylene adipate of acid number 2.5 mg KOH/g. On stirring such a solution bubbles formed

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almost immediately and the total amount of dissolved gas was recovered in less than 1 hour.

It seems possible, therefore, that the slow rate of gas evolution in the first experiments may have been quite unrelated to its rate of formation.

Solubility of Gases in Daltorol

The solubility of carbon dioxide in Daltorol, a modified polydiethylene adipate, has been determined for gas pressures up to 600 mm Hg and temperatures of 35°, 60° and 100°C. It was found that the solubility was directly proportional to the pressure of carbon dioxide under these conditions and the system thus obeys Henry's law. The solubilities at a gas pressure of 600 mm Hg, expressed in ml s.t.p./g, were 1.01 at 35°C, 0.69 at 60°C, 0.43 at 100°C. A linear relationship exists between the logarithm of the solubility and the reciprocal of the absolute temperature.

The solubilities of oxygen and nitrogen in Daltorol have been determined for pressures up to 600 mm Hg and at a temperature of 60°C. Again, in each case, the system obeyed Henry's law. The solubilities at a pressure of 600 mm were: oxygen 0.04 ml s.t.p./g, nitrogen 0.02 ml s.t.p./g.

Dehydration of Polyesters

A programme of work has been started to determine the efficacy of various drying procedures for polyesters. Water contents are being determined by the Karl Fischer method to an accuracy of ± 0.002 per cent.

In the first method examined, about 4000 g. of a trimethylol propane modified polydiethylene adipate was stirred by nitrogen, dried to a water content of about 0.003 per cent and fed through a glass sinter at a flow rate of 300 - 400 ml/min. The polyester was maintained at 60°C and the pressure above the liquid was 15 mm Hg. After 3 hours under these conditions the water content had fallen from an initial value of 0.128 per cent wt/wt to 0.062 per cent wt/wt. After 12 hours and 24 hours the water contents were 0.037 and 0.027 per cent wt/wt respectively.

Kinetic Studies of Urethane Formation

In conjunction with the study of polyurethane formation based on polyglycols or polyesters, and tolylene di-isocyanate, a kinetic examination of the formation of urethane from p-tolylisocyanate and n-butanol at 25° and 40°C was made at concentration ratios of alcohol to isocyanate of 1:1 to 10:1.

The kinetic expression derived by Baker from his proposed mechanism has been examined critically. He assumed that the complex formed between the alcohol and isocyanate was of the van't Hoff type, and hence applied the stationary state treatment to the complex formation.

At high ratios of alcohol to isocyanate, the results obtained in this work, and those obtained by Baker, indicate that the rate of urethane formation is directly proportional to the determined concentration of isocyanate involved in the reaction at any particular time. This suggests that the complex is of the Arrhenius type rather than the van't Hoff type. Using the same mechanism as Baker proposed, an attempt has been made to solve the kinetics of the reaction, assuming the formation of an Arrhenius type complex. A full account of this investigation is in preparation.

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Polyurethane Propellant Processing: General Studies

Improvement in Small (10 lb Batch) Mixing Vessels

The mixing of polyurethane propellants is carried out in two stages: (i) the dispersion of the solid ingredients in the polyester and (ii) the dispersion of a relatively small amount of tolylene di-isocyanate into the initial mix of solids and polyester.

The existing paddle-type stirrers with horizontal breaker bars fitted to the pot wall were found to be inefficient; occasionally cured propellant contained "soft spots" which were deficient in isocyanate. This was considered to be due to the stagnant areas behind the breaker blades.

Several different types of stirrer were investigated, the most successful of which was an anchor type with vertical breaker bar. The blades of the anchor were inclined at 45 degrees to the surface of the mixing vessel, and these have a ploughing action; the lower horizontal blades have a lifting action whilst the vertical ones "pull" the mix from the walls. The breaker bar was hollow and housed a thermocouple. This type of stirrer was found to be more efficient than its predecessor and also to cause a considerable improvement in mix fluidity.

The "Master-Batch" Mix System

In the "master-batch" system a premix is made of several or all the propellant ingredients without the tolylene di-isocyanate. The advantages of such a method are that batch reproducibility should be improved and also that analysis is much simpler than on cured propellant.

A "master batch" of composition U.226 (polyurethane binder 22.5, aluminium 15.0, Ionol 1.0, ammonium perchlorate 61.5) was held at 60°C for one week. The mix was carried out under vacuum for the first day but subsequently the vacuum was released. Samples were withdrawn after 1, 2 and 6 days and made into propellant.

The mix fluidity, polyester reactivity, and perchlorate particle size were checked regularly and found consistent. The burning rate of the uncured propellant in 5 mm glass tubing was determined in the window bomb; there was no evidence of an aging effect with either the cured or uncured propellant.

Magnesium Stearate and Tricalcium Phosphate Anticaking Agents for Ammonium Perchlorate: Effect on Mix Fluidity and Physical Properties of Propellants

To preserve free flowing characteristics in milled ammonium perchlorate and to facilitate blending it has been the practice to add about 0.05 per cent magnesium stearate; this material is compatible with the polyisobutene-bound plastic propellant systems.

However, this magnesium stearate treated perchlorate in polyester polyurethane propellants increased mix viscosity and reduced the extensibility of the cured propellant.

Canadian experience with tricalcium phosphate as an anti-caking agent has been confirmed; in ammonium perchlorate concentrations of T.C.P. above 0.1 per cent were effective and had little effect on mix fluidity or propellant physical properties.

/Effect .....

Effect of Copper Compounds on Gel Time of Polyester Polyurethanes

This study was prompted by the unexpected effect of copper compounds, some of which have been reported as burning rate catalysts, on the cure rate of polyurethane propellants (both T.E.G.D.N. plasticised and non-plasticised). All the compounds investigated cause a considerable reduction in gel time: copper chromite, chromate, oxide, stearate, palmitate, octoate, ricinoleate. The organic salts which are wholly or partially soluble in the polyester have the greater effect, though in an actual propellant mix the pot life with all compounds is too short to permit casting. This is unfortunate as American work indicates that compounds such as copper chromite are specific burning rate catalysts for polyglycol polyurethane propellants.

Effect of Ionol on Mix Viscosity

It has been reported previously that Ionol (di-t-butyl p-methyl phenol) reduces the viscosity of Daltorol propellant mixes. The effect of one per cent Ionol on the viscosity increase after the addition of the tolylene di-isocyanate and on the physical properties of the cured propellant have now been determined. The Ionol was shown to reduce the rate of viscosity increase rather than to reduce the mix viscosity per se. This was confirmed in gel time experiments where the gel time of an unfilled rubber was increased 17 per cent by the presence of Ionol.

The physical properties of the Ionol-containing propellant were similar to those of an almost identical composition not containing the additive.

The presence of Ionol in non-T.E.G.D.N.-plasticised propellants is not an essential to obtain pourable mixes; in fact, its inclusion in a "specified" propellant would undoubtedly cause analytical difficulties, because a large proportion of the Ionol sublimes from the mix during processing. Its vapour pressure is 2 mm at 100°C.

Drying of Liquid Ingredients

An improved drying technique for polyesters and T.E.G.D.N. has been devised, producing lower water contents and reducing propellant mixing time.

The previous method was to "dry" polyester and plasticiser in the mixer for two hours prior to adding the solid ingredients; this two-hour period has been removed from the mixer cycle by drying the ingredients in a separate vessel at 60°C at a pressure of about 5 to 15 mm nitrogen. The nitrogen is bled into the liquid being dried through a sintered glass disc, and effectively stirs it and produces a large surface area. T.E.G.D.N. water content was reduced from 0.46 per cent to 0.007 per cent in two hours; a modified polyester took 24 hours to reach 0.02 per cent water content. In the latter case an increase in temperature to, say, 100°C would reduce the drying time to about 2 hours.

Polyurethane Propellant Processing: Pilot-Scale Facilities

Small-Scale

The new small-scale, humidity-controlled laboratory has been taken over and the five-gallon Beken planetary mixer, four smaller mixers, and the first of three new curing ovens have been installed. With this equipment it is possible to duplicate experiments in formulation, and to scale-up to 50 lb batches capable of filling two 5-inch motors.

/Specification .....

Specifications have been drawn up for ten-gallon mixers of both the planetary and the twin paddle type, and tenders have been invited from suitable manufacturers. As a result of recent experience with the five-gallon planetary type machine, this is no longer considered so satisfactory from the safety and maintenance point of view, and the twin paddle machine is preferred for future operations.

Filling of 5-inch diameter, star-centred motors, 24 inches long, has continued. Short 5-inch coni-cylindrical charges ("J"-rounds) have also been prepared for ballistic assessment, using new filling tools. Several batches of compositions containing T.E.G.D.N. and aluminium have been processed. Trouble encountered with small bubbles was first attributed to moisture in the T.E.G.D.N., but this was shown not to be the cause. The difficulty appears to have been overcome by improvement of the vacuum during mixing, and by an increase in casting time. Further batches of T.E.G.D.N. compositions, cast into motors fitted with inert slivers, now await firing; these should give better performance figures. So far none of the compositions filled into 5-inch rounds has given a measured specific impulse in excess of 233 lb.s/lb (1000 p.s.i./14.7 p.s.i.)

Larger Scale

Proving runs with inert (aluminium/rubber) compositions were completed in the 500 lb vertical mixer, and then 1000 lb batches of uncured live propellant were filled into each of two heavy steel vessels for detonability trials (p. 54)

During these runs, speed and efficiency of mixing were found to be inadequate, and modifications included the fitting of a new "anchor-plough" type of stirrer, new vacuum gland and liquid gland seal. Further inert qualifying runs (using a potassium chloride/rubber mix) were highly successful, and live filling of 17-inch Cuckoo motors was commenced. Five of these motors, containing 420 lb of propellant each, have now been filled successfully, four with an aluminised composition.

So far, the live 17-inch motors examined by radiography and by ultrasonic techniques show sound propellant quality and case bonding. In the case of the inert fillings previously made, this has been verified by sectioning the filled motor.

The motors were made for storage trials, but two (one aluminised) are to be fired at R.P.E. Westcott. An adapted "Raven" endplate, protected with a phenolic capsule filled epoxy resin, is being used on the first, and future endplates with high grade graphite inserts are being prepared. There has been continuous liaison with R.P.E. Westcott and R.A.E. on materials for endplates, nozzles, and thermal insulation, and it is planned to assess a silicon-carbide-coated, nozzle insert in this type of motor.

Short 36-inch diameter mild steel motors, to hold about 1200 - 1500 lb of propellant,have also been procured. Filling tools are all available except for final machining of the mandrel, and experimental incremental filling of these motors for storage trials will commence shortly.

Fillings for Detonability Trials

During the course of this gradual scale-up of operations, each stage has been accompanied by detonability trials designed to assess the type of risk involved and the nature of the personnel protection required.

/Eight .....

Eight heavy steel vessels, having a bursting pressure around 2000 p.s.i., were each vacuum filled with 100 lb of cured aluminised propellant. These charges in fairly heavy confinement were subsequently initiated either by heating over Avtag fires or by detonators placed internally; some of the charges were preheated. Only pressure bursts were observed, confirming earlier results on partially mixed uncured materials.

Further confirmation of very low order detonations, corresponding in blast pressures to less than 2 lb of P.E., was obtained from similar experiments with 1000 lb batches of uncured propellant in ¼-inch steel vessels, simulating large-scale mixer conditions.

New Large Scale Project

The existing 500 lb facility, while adequate for gaining the necessary experience in the filling of 17-inch and larger motors, is far from suitable for incremental filling on a semi-production basis of the large motors required for development and acceptance for Service of a particular missile. A plant was needed having rapid mixing cycle, more efficient handling of the large quantities of ingredients(especially perchlorate), and also remote control for safe operation.

Such a plant is now at the planning stage, based on a new mixer by Baker Perkins who will be responsible for its design and construction. The mixer will have twin helical paddles intermeshing in a figure-of-eight bowl, and will be largely self-cleaning. Experiments carried out at the works at Peterborough with a smaller mixer of similar design promise a very rapid mixing action with a high degree of safety. The new mixer should be capable of producing a 700 lb batch every 1½ to 2 hours, for filling motors of up to one ton capacity.

XXI.6 COMPOSITE PROPELLANTS

Deformation of Plastic Propellant Under Small Stresses

Recent work on the rheology of plastic propellant has been concentrated on attempts to predict the tendency of large motors to slump. Constant load shear and tensile tests have been carried out on further compositions, and their behaviour studied at stresses near the yield point. An observed linear relation between stress and reciprocal breaking time for long breaking times has enabled extrapolation to infinite breaking time to be made with confidence. The yield tensile stress varies threefold over the range of compositions studied; thus the maximum possible charge diameter depends markedly on the type of propellant used.

For studying the extent of slumping at stresses below the breaking stress, a simple cantilever beam bending test has been devised. A cylinder of propellant is held with its axis horizontal, one end free, and the other stuck to an end plate. The sag at the free end is measured when no further deformation takes place; by using differing lengths of beam, the relation between bending stress and apparent modulus can be determined. Advantages of this test system include its simplicity, and the fact that the propellant is slumping under its own weight, and not under externally applied stresses. In the bend test, the shear stress is negligible compared with the bending stress; in a rocket motor the reverse is the case. The extent to which the classical relations between Young's Modulus

/and .....

and shear modulus apply to plastic propellants is not known. Within these limitations, however, the cantilever test gives useful predictions of slumping behaviour. For example, for propellant E.3668, test results predicted a maximum slump of 3 cm for the 3-foot test vehicle; after 4 days the observed slumping was 2.5 cm. For propellant E.3611 the agreement was not so good, owing apparently to the age hardening of this propellant.

Expressions for the deformation due to shear and to bending stresses for short motors with cylindrical conduits have been derived. For the E.R.D.E. 36-inch test system, the bending deformation is greater than the shear deformation; in a rocket motor, the bending stresses will be very small, and the deformation will therefore be only about half that in the test system.

2-inch diameter K-rounds, filled with propellant E.3668, were subjected to accelerations from 40 to 100 g in a large-capacity centrifuge. At 40 g there is incipient adhesion failure after some hours; at 50 g adhesion failure begins in 30 minutes. At 60 g some slumping occurs, and at 80 g slumping is serious, after 15 minutes. Values of the apparent shear modulus obtained from these and other similar tests are being compared with values obtained from cantilever bend tests and other tests described previously.

The deformation of small motors spun about their own axis is also being studied.

Thermal Expansion of Composite Propellants

The thermal coefficients of cubical expansion of a number of composite propellant ingredients have been determined. The results are as follows:

TABLE 3

Substance	10^5 x Cubical Expansion Coefficient in (deg. C)$^{-1}$		
	20° - 40°C	40° - 50°C	40° - 60°C
Oxamide	13.48	13.46	
Ammonium perchlorate	18.40	16.46	
Ammonium picrate	20.28	16.48	
B146 (polyisobutene/ ethyl oleate)	62		62
Polyurethane rubber, 100/9 Daltorol/T.D.I.	71.6		71.2
Polyurethane rubber, 5/13.6/1.24 T.E.G.D.N./Daltorol/ T.D.I.	80.4		81.6

Assuming that thermal expansion is an additive property for the propellant, values for plastic propellants range from 24 to 27.5 x 10^{-5}; for polyurethane propellants the range is from 32 to 39 x 10^{-5} (deg.C)$^{-1}$.

/The .....

The Aging of Plastic Propellant

Further studies have been made on the age hardening of certain plastic propellant compositions. Propellant E.3668, supplied for the R.P.E. 36-inch motor, has been found to harden in a manner similar to compositions previously studied, but to a less extent. In constant load tensile tests, the breaking times were least, and the elongations greatest, immediately after pressing. Previous history has no effect on the rheology. The propellant hardens after one day; the rate is the same at +20° as at +60°C, but is faster at -20°C. Re-pressing at the lower temperature does not reverse the effect.

Several possible causes of age hardening have been studied, including both physical and chemical effects. The results for E.3688 suggest that a major cause is differential thermal expansion between binder and filler. In plastic propellants, the binder expands four times as much as the oxidants; in polyurethane propellants the factor is five times. Thus, when the propellant is cooled, the binder contracts more than the solids; for systems with low solid concentrations, the inter-particle distances would simply be reduced. For highly loaded systems, where this is not possible, either the binder must be drawn up into the interstices, or de-wetting must occur. A simple calculation, based on a very crude model for plastic propellant, has indicated that, because of the high viscosity of the P.I.B. binder, the stresses induced by the flow are greater than the breaking strength of the binder, or the strength of the binder-crystal bond, even at quite low cooling rates. Thus de-wetting and the formation of voids will be expected to occur, with a temperature change in either direction, when the overall temperature is low.

The effect is not entirely disadvantageous; filled motors which need to be protected from distortion after pressing often cease to need this protection after 24 hours.

The Effect of Confining Pressure on Mechanical Properties

It has been found that polyurethane propellants show pressure effects which are in some cases greater than those previously reported for plastic propellants. Thus tensile test pieces of Composition P5, subjected to constant load, broke in 22 seconds in vacuo, 30 seconds at atmospheric pressure, and were unbroken after a day at 30 atmospheres confining pressure.

A second apparatus has been constructed, for tests at constant strain rate in the range 0 - 8 atmospheres. Compression tests on propellant P2 showed that confining pressure increased the modulus, compressive strength and compression to break. The type of break was also different; under pressure clean shear fracture occurred at an angle of 35° to the axis, and secondary fractures, which were observed at atmospheric pressure, were absent.

Constant rate tests confirmed previous constant load observations that colloidal propellants show no pressure effect over this range of confining pressure.

Compressibility studies (see next section) have shown that composite propellants contain up to 0.2 per cent of either air or voids, and that the pressure required to close these voids is similar to that required to complete the pressure effect on mechanical properties.

The thermal diffusivity of plastic propellant E.3668 has been measured at atmospheric pressure and 60 atmospheres confining pressure. The diffusivity is about 10 per cent lower under pressure. Presumably the voids

/act .....

act as a thermal barrier at atmospheric pressure.

The Compressibilities of Composite Propellants

Measurements have been made of the compressibilities of plastic and polyurethane propellants over the range 1 to 8 atmospheres, in a simple glass apparatus. For plastic propellant, compressibilities at up to 70 atmospheres have also been studied by measuring the volume change when the propellant is consolidated in a cylindrical mould. Typical compressibilities, measured from the linear portion of the pressure/volume graphs, were 4×10^{-5} atm.$^{-1}$ for plastic propellant E.3668 and 3×10^{-5} atm.$^{-1}$ for polyurethane. At low pressures however, the compression is greater, owing to the consolidation of small voids. The void volume varies from sample to sample, and represents up to 0.2 per cent of the total volume. It reappears when the pressure is released; the voids are therefore naturally present in material in equilibrium. They are unlikely to affect the operation of the propellant in a rocket motor, but have an important influence in its rheological behaviour.

Polyurethane and High Energy C.D.B. Propellants: Study of Volume Changes on Straining

The volume changes which occur when polyurethane and high-energy cast double-base propellants are subjected to tensile or compressive strains have been investigated with the E.R.D.E. rheohydrometer. An increase in volume occurs whether the strain is tensile or compressive, and is due to de-wetting of the binder from the filler. The volume increase usually begins at a strain of about 25 per cent, and the void volume reaches a maximum of about 5 per cent at a strain somewhat lower than the breaking strain. In this region, the volume changes are time dependent, since stress relaxation processes are tending to close the voids.

In compositions which do not contain aluminium, "blanching" of the propellant occurs at the stage where the volume increase begins. As the temperature is raised, the volume increase becomes smaller, and the effect is more time dependent.

/XXII .....

XXII PROPELLANTS FOR ORDNANCE

XXII.1 NEW EQUIPMENTS

40 mm L.70 Gun

A.R.D.E. interest in the cool 19-hole F.527/203 composition has diminished in view of the puzzling, rather high rate of wear at the muzzle with this propellant. A further wear trial is to be carried out, under N.A.T.O. supervision, of N/M 024 with the rounds having a higher bullet pull than previously. A 19-hole propellant F.527/224, which is the F.527/203 composition modified by the addition of 1 per cent each of cupric oxide and "lead stannate", has shown a very small temperature correction when fired in the gun over the range -40° to 120°F (-40° to +49°C).

105 mm Tank Gun

The Service propellant for this gun is NQ/M 044. This composition has been made in both 19 and 37-hole granule form, with a mean web of about 0.037 inch. Gun firings have indicated that the 19-hole propellant gives a slightly reduced temperature correction over the range -40° to +120°F compared with the 7-hole Service propellant, while the 37 hole propellant gives a still smaller temperature correction for the range -40° to 70°F, with a more normal trend for 70° to 120°F (+21° to +49°C).

Propellants for the 81 mm Mortar

The readily available small grain sporting and rifle powders did not completely meet the difficult propellant problems posed by the new A.R.D.E. 81 mm mortar. Assistance has been given on the ignition system of the primary cartridge. A.R.D.E. had obtained promising results by mixing magnesium with a nitrocellulose powder and similar properties with a single powder were desired. An experimental double-base composition F.452/282, containing 30 per cent N.G. and 29 per cent aluminium, in disc form 0.013 inch thick, were tried. Results of firing tests at -40°F were encouraging ballistically, although some smoke was produced. It was felt that a lower aluminium content and a smaller web size were necessary. Six further batches containing 10 or 20 per cent aluminium were then supplied in the form of discs and tubes 3 inches long.

First assessment indicated that the two compositions with 10 per cent aluminium gave much better regularity than the NPP 10 powder at present used. The venting pressure of the primary cartridge will also depend on the bursting strength of the container and the venting area. Three conventional compositions of high calorimetric value have been processed in tubular form for use with thicker containers and one, F.452/376, 0.017 annulus proved satisfactory in 3-inch lengths.

Assistance is also being given to A.R.D.E. in the selection of the most suitable secondary propellant to give 805 ft/s within a pressure of 4 ton/inch^2. The final choice between a sheet propellant and granular propellant has not yet been made although a porous I.C.I. powder was selected for first trials. To give further information on the reproducibility of porous powders, which might be necessary for good wet performance, a range of disc nitrocellulose powders with porosities in the range of 0 to 30 per cent has been made and the powders are awaiting assessment.

/Samples .....

Samples of our small-grain uncoated ball powder, from an intermediate stage of the ball powder process, and discs of sheet HSC 0.008 inch thick have given good ballistic regularity under dry conditions. The final choice of secondary propellant will be dependent upon the results of wet efficiency assessments.

/XXIII .....

XXIII PROPELLANTS FOR SMALL ARMS

XXIII.2 BALL POWDER

Ballistic Stability on Storage

For a number of years the ballistic stability on storage of commercially manufactured ball powder has been regarded as poor. It was concluded from previous storage trials (QTR.4/58) that the time and temperature of moderation were the major factors in determining ballistic stability. To give further information, two batches of nitroglycerine-impregnated base grain were prepared:-

(a) E.R.D.E. type - guncotton base grain, boiled in water, nitroglycerine-impregnated in water for 4 hours at 60°C.

(b) Olin type - base grain from blended 12.6 and 13.4 per cent nitrogen, mechanically nitrated cotton, nitroglycerine-impregnated in water containing ethyl acetate and maintained for 4 hours at 75°C, followed by vacuum distillation for 5 hours at 75° - 80°C. This use of solvent at the impregnation stage is said to assist penetration of the nitroglycerine into the ball.

Each type of base grain was divided into six batches which were moderated with about 6 per cent dibutyl phthalate under similar conditions in an incorporator for 1½, 2¾ and 4 hours at 90°C and 6, 11, and 16 hours at 70°C. The powders were stored in bulk in sealed metal containers which were withdrawn for ballistic assessment by D.I.Arm, Swynnerton, in the 7.62 mm rifle after 1, 2 and 3 months storage at 160°F (71°C). To avoid confusion in the interpretation of results, a magazine stored sample of each variant was fired at the same time as the hot-stored sample.

A sample of an early pilot-scale batch of Bishopton ball powder was used as a ballistic and storage control. It was not possible to indent the cartridge cases for these firings so that observed velocities were some 100 ft/s below specification, but this does not affect the validity of the results.

The conclusions drawn are:

(i) Moderation with dibutyl phthalate at 70°C gives poor ballistic storage properties with the Olin type ball powder, and the pressure rises of 5 to 8 tons/inch^2 after 1 to 2 months storage at 160°F are similar to those given by early batches of Olin (East Alton) ball powder obtained from U.S.A. Better storage properties would be obtained by moderating this base grain at 90°C but appreciable pressure rises of 1 to 2 tons/inch^2 still occur in 3 months at 160°F.

(ii) The E.R.D.E. base grain may be moderated at either 70° or 90°C to give stable powders. This type of powder is less affected by storage than Olin type powder and even after 3 months storage at 160°F, the pressure changes are all well under 1 ton/inch^2. This is attributed to the use of guncotton rather than blended cotton nitrocellulose and also to the absence of solvent during nitroglycerine impregnation.

(iii) The pilot-scale sample of Olin ball powder made at Bishopton by the Badger process has behaved surprisingly well on storage and it will be instructive to confirm reproducibility with the larger scale batches.

/Microscopic .....

Microscopic examination of the samples before storage showed that the Olin type powders moderated at 70°C had a much thinner rind than those moderated at 90°C or the E.R.D.E. type powders moderated at 70° or 90°C. An examination of some of these powders after 1 months storage at 160°F has shown little change in rind thickness except for the Olin type moderated at 70°C, for which the rind thickness has doubled.

R.O.F., Bishopton has been requested to manufacture samples of ball powder moderated at higher temperatures for various times to enable further confirmatory storage trials to be conducted.

/XXIV .....

XXIV LIQUID PROPELLANTS

XXIV.1 HYDROGEN PEROXIDE

The System Al - H.T.P.

The corrosion of metallic aluminium in H.T.P. has been further studied by examining the changes in weight and the electrode potentials of immersed strips, and by determining the electrical resistance of the oxide films on the metal surfaces. It has been possible to distinguish between the electrochemical corrosion of metallic aluminium, in which aluminium oxide is formed, and the purely chemical solution of aluminium oxide which leads eventually to the adsorption of aluminium ions on the surface of the stannic acid stabilizer. These two reactions are affected differently by variation of conditions. The electrochemical reaction is accelerated by chloride and hydroperoxyl ions, and is repressed by nitrate ions. On the other hand, the chemical solution is enhanced by a higher acid concentration and by the presence of stannic acid sol. It is only the chemical reaction which transfers aluminium ions into the liquid phase and so brings about the precipitation of the stannic acid.

It is now believed that the adjustment of the surface reaction

$$Al_2O_3 + 3\,H_2O \rightleftharpoons 2\,Al^{3+} + 6\,OH^-$$

is rapid and reversible, but that the Al^{3+} ions remain in a surface layer since the reaction $Al^{3+}_{surface} \rightarrow Al^{3+}_{solution}$ has a high activation energy and is irreversible. However, stannic acid sol particles have the power to drag adsorbed aluminium ions through the potential barrier following collision with, or penetration into, the surface layer by the colloid particle. When sufficient aluminium ions have been removed to precipitate the sol, the means for passing through the energy barrier are no longer available and solution of aluminium ions sensibly ceases.

The Solution Chemistry of Sodium Stannate

(a) Manganese Titration

This technique, which is a rapid method of determining the reserve stabilizing power of stannic acid colloid in H.T.P., was developed from a method being used at the De Havilland research laboratories. It is briefly as follows. Addition of manganous ions to H.T.P. in contact with silver wire produces, after an initial period of constancy, a sharp increase in the rate of oxygen evolution. Further addition reduces the gas rate and it has been shown that the position of the peak is proportional to the amount of stannic acid colloid present in the system. The position of the peak may also be shifted by the addition of small quantities of other ions such as Al^{3+}, and it is believed that the manganese titration value may be directly related to the number of free adsorption positions which are present rather than the amount of the colloid itself. This method has found application in a number of problems related to the stabilization of H.T.P.

(b) Precipitation of Stannic Acid Sol by Aluminium Ions

The manganese titration technique already described, together with turbidity measurements and chemical analysis, provides a means of studying

/quantitatively .....

quantitatively the precipitation of stannic acid colloid by aluminium ions.

Using stannated H.T.P. which had been allowed to age for one month (see below) it was shown that a 30 mg/l colloid was completely precipitated by 0.4 mg/l of aluminium; incipient precipitation was observed with only 0.2 mg/l of aluminium. Precipitation was complete after 4 hours. However, stannic acid thus precipitated is capable of adsorbing additional aluminium ions, in a less firmly-bound condition, and further examination showed that 30 mg/l of stannate could retain a total of about 2 mg/l of aluminium ions. It seems likely that the "second stage" adsorption is due to van der Waals-London forces.

This investigation is being extended to the precipitating effect of ferric ions.

(c) <u>The Aging of Stannic Acid Sols in H.T.P.</u>

The differences in the nature of stannic acid sol particles formed in water and in H.T.P. have been emphasized in QTR.2/59. Aging, an important property of aqueous sols, is much less apparent in hydrogen peroxide. However, some indication that an aging process exists even in H.T.P. was given by electron microscopy and mentioned in QTR. 3/59. Two techniques have been used to study this aging process quantitatively. Both depend on the power of a sol to adsorb polyvalent cations, one being the "manganese titration" method described above, and the second being a refined "reserve stabilizing power" test involving the addition of ferric ions to the system and observation of the degree of deactivation produced by the sol.

Both methods indicated that on storage (in polythene) an aging process definitely takes place, resulting in a drop of approximately 25 per cent in the adsorptive power of the sol during the first two weeks following preparation. After this time the adsorptive power remained relatively constant. It would appear advisable to leave stannic acid sols to mature for a few weeks before use, since a more reproducible material will thereby be obtained.

<u>The Catalytic Decomposition of H.T.P.</u>

A "D.C.L." Null Balance Oxygen Analyser has been used in a study of the decomposition of H.T.P. in the presence of catalytic cations. The variation in the rate of oxygen evolution from the time of the first addition of catalyst until a steady reading was obtained clearly indicated that, whilst iron and copper were present in a heterogeneous form, the catalysis by chromium was homogeneous.

In the case of iron and copper, peaks in the gas evolution curve were obtained a few minutes after addition. With iron the peak occurred from 15 to 25 minutes after addition, falling to a reasonably steady rate after about 5 hours. The addition of 30 mg/l of sodium stannate to 1 mg/l. of Fe^{3+} at either the peak or the steady rate showed effective stabilization to be complete within 30 minutes. The peak for copper came more quickly, about 5 minutes after addition, but after 40 minutes a very low steady state was reached, at which stage the copper had precipitated out and was almost non-catalytic.

Cr^{3+} and Cr^{6+} gave steadily increasing rates until a steady state was reached after about 60 minutes in each case.

/XXV .....

XXV INTERNAL BALLISTICS RESEARCH

XXV.2 EXPERIMENTAL STUDIES ON FLAME PROPAGATION AND COMBUSTION MECHANISMS

The Role of Alkyl and Alkoxyl Radicals in the Pyrolysis and Combustion of Alkyl Nitrates

The initial formation of alkoxy radicals in the pyrolysis and combustion of alkyl nitrates is well known, and it is generally accepted that these free radicals can further undergo C-C or C-H bond fission, at suitably elevated temperatures, to form alkyl radicals or hydrogen atoms. From studies on the decomposition flames of alkyl nitrates it has been argued that the small yields of methane, the normal product of reaction of methyl radicals with organic compounds via hydrogen abstraction, indicate that alkyl radicals undergo other more rapid reactions, in particular oxidation by or addition of nitrogen dioxide.

It has now been shown that methyl radicals undergo a rapid reaction of a novel type with alkyl nitrites, which themselves are intermediate products in the pyrolysis or combustion of alkyl nitrates

$$\overset{\bullet}{CH}_3 + RONO \rightarrow CH_3NO + RO. \qquad \ldots\ldots \underline{1}$$

Thus methyl radicals from the pyrolysis of di-t-butyl peroxide react rapidly with methyl nitrite at 160° - $180^{\circ}C$ to give formaldoxime (via nitrosomethane and isomerisation), methanol and an unidentified high-boiling reddish-brown oil. The probable reactions are

$$\overset{\bullet}{CH}_3 + CH_3ONO \rightarrow CH_3NO + CH_3O\cdot \qquad \ldots\ldots \underline{2}$$

$$CH_3O\cdot + CH_3NO \rightarrow CH_3OH + \cdot CH_2NO \qquad \ldots\ldots \underline{3}$$

$$\cdot CH_2NO + \cdot CH_3 \rightarrow \cdot CH_2NOCH_3 \rightarrow (CH_2NOCH_3)_x \qquad \ldots\ldots \underline{4}$$

in which the oil results from radical addition to the products of methoxyl attack on nitrosomethane. Similar results are obtained when methyl radicals are reacted with ethyl and isopropyl nitrites.

Reactions of this type in which alkyl radicals abstract a group in preference to a hydrogen atom are very rare, and a note on this work has been published in the open literature. It is evident that these reactions are of importance in the combustion of alkyl nitrates, and a kinetic study is planned.

It might be expected by analogy that methyl radicals would attack the NO_2 group from alkyl nitrates. Analysis of the products of reaction of methyl radicals (from the pyrolysis of di-t-butyl peroxide) with ethyl nitrate at 160° and $180^{\circ}C$ show that in addition to hydrogen abstraction

$$\cdot CH_3 + CH_3CH_2ONO_2 \rightarrow CH_4 + CH_3CHO + NO_2 \qquad \ldots\ldots \underline{5}$$

followed by

$$\cdot CH_3 + NO_2 \rightarrow CH_3NO_2 \qquad \ldots\ldots \underline{6}$$

and

$$\cdot CH_3 + NO_2 \rightarrow CH_3O\cdot + NO \qquad \ldots\ldots \underline{7}$$

/a .....

a significant amount of ethyl nitrate is decomposed by either or both of the reactions:

$$\cdot CH_3 + CH_3CH_2ONO_2 \rightarrow CH_3NO_2 + C_2H_5O\cdot \quad \ldots\ldots 8$$

$$\cdot CH_3 + CH_3CH_2ONO_2 \rightarrow CH_3O. + CH_3CH_2ONO \quad \ldots\ldots 9$$

The direct reactions with ethyl nitrate are, however, much slower than the abstraction of the NO group from nitrites by methyl radicals.

A study of the pyrolysis of isopropyl nitrite has been carried out using a static-type apparatus, with the aim of characterising the reactions of the initially formed isopropoxyl radical. These appear to be

$$(CH_3)_2CHO. + NO \rightarrow (CH_3)_2CO + HNO \quad \ldots\ldots 10$$

$$(CH_3)_2CHO. + HNO \rightarrow (CH_3)_2CHOH + NO \quad \ldots\ldots 11$$

$$2(CH_3)_2CHO. \rightarrow (CH_3)_2CHOH + (CH_3)_2CO \quad \ldots\ldots 12$$

$$(CH_3)_2CHO. \rightarrow CH_3. + CH_3CHO \quad \ldots\ldots 13$$

The splitting of the isopropoxyl radical into a methyl radical and acetaldehyde is, as already stated, a type of reaction of considerable importance in the pyrolysis of alkyl nitrates. Analysis of results suggests an activation energy of about 28 kcal/mole for this reaction, but the significance of this value is questionable because of difficulties in the precise analysis, by infra-red methods, of the complex products. Work now in hand using gas chromatography suggests that more reliable results can be obtained.

XXV.3 SOLID SYSTEMS

Ammonium Perchlorate Combustion: Burning Surface Temperature Measurements

The spectral emissivity of ammonium perchlorate has been measured in several wavelengths in the infrared, as a function of temperature over the range $180^\circ - 360^\circ C$. Using the values obtained and measuring the energy radiated at these wavelengths from surfaces of ammonium perchlorate burning at atmospheric pressure, surface temperatures have been obtained. It is found that the surface temperature remains constant at $500^\circ \pm 17^\circ C$, although the rate of burning may be increased six times by small additions of fuels or catalysts. The chemical nature of the fuel, so far as is known at present, makes no difference to the observed temperature, nor does the presence of a strong burning rate catalyst such as copper chromate. Preheated perchlorate, containing no fuel, also gives the same surface temperature. If the process at the surface is sublimation, governed by the rate of heat input, the surface temperature would be expected to remain constant irrespective of burning rate at any one pressure but to increase with pressure, whereas if decomposition reactions take place upon the crystal surface, an increase in temperature would be associated with an increase in rate. There is some evidence that the surface temperature does increase with pressure.

Thrust Efficiency of Aluminised Propellants

Some of the conclusions regarding the thrust efficiencies of certain double-base and polyurethane propellants containing low concentrations of aluminium have had to be modified subsequent to the discovery that the

ABL short method of computing the theoretical impulse is in error for the cooler compositions. A more reliable quick method has been devised and is now in use.

This method is based on interpolation procedure, which makes use of maintained-equilibrium performance data obtained by rigorous computation. Two equations, with accuracies of 0.5 and 0.7 per cent, have been obtained; one is applicable to all practical high-energy aluminised solid propellants, the other to all types of high-energy propellants with specific impulses in excess of 270 lb.s/lb. Each calculation involves the estimation of three variables, Q (the heat of reaction at 298°K), n(the number of moles of gaseous product), and c (the heat capacity of both solid and gaseous products at 2000°K). A calculation can be performed in 10 minutes, and, in addition, both the chamber and exhaust temperatures can be estimated quickly to within 50°K.

With the theoretical impulse values now readily available for a range of propellants of different types, better assessment of the thrust efficiencies of aluminised propellants, with respect to propellant chemistry and test motor design, is possible. It may now be said that, in 2-inch K-round firings, both C.D.B. and plastic propellant maintain or show only a slow reduction of efficiency (in the region of 95 - 93 per cent) for aluminium concentrations up to about 15 per cent provided that the propellant matrix carrying the aluminium is of high energy and burning rate. Above this aluminium concentration a more rapid drop in thrust efficiency is experienced. In plastic compositions progressively cooled with ammonium picrate to reduce the burning rate, the efficiency falls and the rapid fall-off with metal content occurs at progressively lower aluminium concentrations.

Polyurethane propellants, which are also of comparatively low burning rate, also give thrust efficiencies which are low both with or without metal addition.

It would seem to be generally true that the higher the rate of burning and the higher the propellant matrix energy, the more efficient is the utilisation of the aluminium, other conditions being equal. The reason for this may lie in conditions at the burning surface of the propellant, which have been shown to influence the size of the aluminium globules thrown into the flame gases. These globules are frequently very much larger than the aluminium particles put into the propellant and it is very unlikely that the original state of division is of very great importance. More important factors are likely to be those which influence the thickness of the flame zone and the associated depth of heating of the surface, e.g., rate of burning, heat of reaction, pressure. Changes in rate and pressure have been shown to produce gross changes in the size of aluminium globules ejected from the surface. The low efficiencies at low burning rates may also be due in part to thermal losses to the motor body and nozzle. Loss of energy to the walls of the motor is significantly larger with these slow-burning compositions and the corrections that should be applied are being examined in relation to the energy and rate of burning of the particular composition.

Laboratory Studies of the Combustion of Light Metals

The oxidation of individual particles of metals in a variety of hot atmospheres may be studied, with quite high time resolution, by injecting the particles through a premixed flame of known composition and flame speed. Experiments have shown that oxidation is very much more rapid in atmospheres of CO_2 and H_2O containing small amounts of free O_2 than in those

/without .....

without. The oxidation of an individual aluminium particle in slightly fuel-rich flames (i.e., no residual O_2) is, in fact, so slow that no precise termination can be observed before the particle leaves the top of the flame. If, however, a high concentration of aluminium is introduced, there is a rapid, apparently vapour-phase, oxidation.

In a flame containing some residual oxygen, the phases of combustion of an aluminium particle may be distinctly observed: (a) ignition, (b) steady burning, (c) "explosion" or bursting of the burning particle. In all mixtures the ignition delay increases with particle size, is dependent upon the flame temperature, yet is little affected by gas composition. The burning time, on the other hand, is more dependent upon oxygen concentration than on temperature of the surrounding flame. Diffusion of oxygen may be rate-controlling but the "explosion" of the particles (when oxygen concentration is high) shows that steady-state conditions are not attained. Unsymmetrical accumulations of oxide around the particles may account for the observation that the latter burn over part of the surface only. This concept may be linked with the observation of high-speed rotation (ca. 12,000 rev/s.) of the burning particles.

Differences in reactivity of metals may be demonstrated by significant changes in ignition delay for a given size of particle. For example the delays for 53 - 66 μ particles of Ti, Mg, Mg/Al, and Al metals in a CO/O_2 flame (flow ratio 1:1.27, temperature 2800°K) are respectively 0.9, 1.8, 3.4 and 5.9 milliseconds at atmospheric pressure.

Strand Burning Rates of Polyurethane Composite Propellants at High Pressures

An investigation has been undertaken to determine the pressure/rate relationships of some polyurethane composite rocket propellants up to pressure of 15,000 p.s.i. The measurements were carried out in the high pressure hydraulic strand burner. Two composite propellants were investigated: U 89/D4 [NH_4ClO_4, 80; Daltorol, 18.2; T.D.I., 1.8] and U 188 [NH_4ClO_4, 65; Daltorol, 13.76; T.D.I., 1.24; T.E.G.D.N., 5; Al, 15] using 3/16-inch square strands.

The strands could not be ignited under water below 7000 p.s.i. Above this pressure the linear burning rate appeared to increase with pressure with an exponent greater than unity, (see Table 4). Although variation in inhibiting technique did not reveal any side burning effects which might cause spuriously high pressure exponents, the results are open to doubt until confirmed in Closed Vessel firings. These are being made, with investigation of the behaviour of other composite propellants in the hydraulic strand burner.

/TABLE 4 .....

TABLE 4

Propellant:	U.89/D4		U.188	
Pressure, p.s.i.	R_B, inch/s	Slope of Log/Log Plot	R_B, inch/s	Slope of Log/Log Plot
7,000	0.62	0.81	0.9	0.92
8,000	0.70	1.0	1.04	1.23
9,000	0.80	1.34	1.2	1.33
10,000	0.98	1.9	1.4	1.4
11,000	1.2	2.5	1.6	1.7
12,000	1.5	2.8	1.9	2.1
13,000	1.9	3.4	2.25	2.4
14,000	2.4	3.8	2.7	2.6
15,000	3.0	-	-	

Assessment of Materials for Use as Nozzles and Chokes in 2-inch K-round Motors

Comparative trials have been carried out in 2-inch K-round motors to find materials giving minimum erosion with high-energy solid propellants. The materials examined to date consist of:

(i) 13 grades of commercial unimpregnated carbon,

(ii) 4 grades of carbon prepared by the Metallurgical Department, R.A.E. Farnborough,

(iii) Molybdenum.

Test specimens are in the form of flat discs, ¼ inch in thickness, and containing a central hole. These were used as choke plates in 2-inch K-round motors. The relative increase in cross-sectional area of this hole was used as an index of performance of the material.

Two polyurethane propellant formulations were used, U.216 [NH_4ClO_4, 72.5; rubber, 15.75; T.E.G.D.N., 6.75; aluminium, 5.0; Tc = 3200°K] and U 241 [NH_4ClO_4, 60.0; rubber, 15.0; T.E.G.D.N., 5.0; aluminium, 20.0; Tc = 3550°K].

The three commercial carbon grades giving lowest erosion were:

(i) Le Carbone - Grade P.5890,

(ii) National Carbon - Graphite ATJ,

(iii) Nobrac Carbon - Grade M.3.

Of the four carbon grades prepared by R.A.E. Farnborough one was comparable in performance to the commercial grades. Molybdenum showed little or no erosion with propellant U.216 but was inferior to the best carbon grades with propellant U.241.

/Internal .....

Internal Ballistics of 127-hole Perforated Charge for the Travelling Charge Gun

The burning of sections of an extruded 127-hole perforated charge for the Travelling Charge Gun, manufactured experimentally at E.R.D.E., was studied; the ballistic parameters obtained by burning short sections of the charge in the Closed Vessel were compared with those obtained with the same propellant in cord form. Considerations of the geometry of the sections enabled a hypothetical form function to be derived which was used in interpreting results obtained with Closed Vessel. The form function for the sections was

$$Z = (1 - f)\ (1 - 0.20\ f)$$

where Z = the fraction of charge burned away at any time t,

f = the fraction of web burned away at time t,

and, in the ballistic equations, value of "1.147D" was used instead of D for the web thickness.

The burning rates deduced from the firings indicate good agreement between charge and cord up to a pressure of 5 tons/inch^2. From 5 to 10 tons/inch^2 there is a slight divergence, the value for - Ddf/dt at the same pressure being smaller for the charge than for the cord. As far as can be judged, the sections of the perforated charge burned normally over the pressure range explored and there was no erosive burning in the ¾-inch length sections examined.

/XXVI .....

XXVI SENSITIVENESS AND DETONABILITY OF PROPELLANTS, HIGH EXPLOSIVES AND INITIATORS

XXVI.1 EVALUATION OF THE SENSITIVENESS OF EXPLOSIVES AND PROPELLANTS

Trials on Polyurethane Propellants

The trials reported in QTR.3/59 on vessels holding 100 lb of polyurethane propellants were continued on the scale of 1000 lb of fully mixed but uncured P2 propellant, in each of two vessels built to represent the incorporators in which propellant would be mixed in batches of 1000 lb. One of the two vessels was heated over a fire of Avtag fuel while in the other a 7 g. SR371C igniter was fired below the surface of the propellant, which in this vessel was preheated to about 180°F (82°C) since the propellant is mixed hot. The first vessel gave a very mild explosion with no measureable blast, while the second produced blast equivalent to only about 3 lb of plastic explosive.

At the request of D.S.S., further trials were carried out on fully-cured polyurethane propellants P2 and U322, to investigate the risks arising in storage and transport of filled rocket motors. The trials were done on the 100 lb scale, in 12-inch diameter vessels similar to those described in QTR.3/59, since the greater confinement in the 100 lb vessels had resulted in the production of slightly more blast than that from the 1000 lb vessels which were of weaker construction. The vessels and propellant were preheated to about 60°C to simulate the temperature in the curing oven. Four vessels of each propellant, and two containing ammonium perchlorate for comparison, were heated over Avtag fires. Only "very mild explosions" were produced; the highest blast effect from any container was estimated as equivalent to 3.1 lb of P.E.

On the basis of these results it is considered that the propellants after filling into rockets can be regarded as a "Y" risk, and that the mixing and filling processes can also be treated as a "Y" risk provided that the operatives are protected from fragments. This series of trials is reported in detail in E.R.D.E. Technical Memorandum No. 6/M/60.

Burning to Detonation in Casting Powders (QTR.2/59)

The minimum shock pressure for the initiation of detonation in high-energy casting powder F.452/229, confined in six-inch long steel tubes, has been determined by projectile impact methods. A suitable range of low projectile velocities was obtained by the use of a Browning 0.5-inch barrel. The results of an investigation into the effects of charge and projectile diameters are not as simply interpretable as were those obtained with high explosive charges. The 50 per cent velocity for half-inch diameter steel projectiles increased linearly with charge diameter up to about 2¾ inches, above which it remained constant. The critical pressures found by using projectiles of varying shock impedances varied between 8 and 15 kilobars for a range of projectile diameters. The critical length of projectile is greater than 0.5 inch in all cases.

Gap tests with explosive donor charges on E.R.D.E. Scale VI showed that the length of charge required for detonation varied with the strength of initiating shock. For a range of powders of different energy levels the length required for detonation with a fixed shock strength correlated with the ease of burning to detonation.

Measurements are being made of the transient pressure developed during burning to detonation.

/XXVI.2 .....

XXVI.2 FUNDAMENTAL STUDIES OF EXPLOSIVE INITIATION PHENOMENA

The Transition from Shock Wave to Detonation

Charges of RDX/TNT have been initiated by an incident shock wave in such a way that the transition to detonation occurred an appreciable distance from the entry face. The course of this transition has been observed by measurements of the surface shock and particle velocity. Three sizes of charge have been used, and in a proportion of the experiments the charges were made up of layers separated by metal foil, the direction of motion of the shock being at right angles to the layers.

It was found that:

(i) With charges 15 mm square cross-section by 38 mm long, the shock intensifies for about 20 mm prior to detonation, and in no case does the ensuing detonation propagate in the direction counter to the shock.

(ii) With charges 75 mm square cross-section by 200 mm long, the shock does not appear to intensify at all prior to detonation, and the detonation propagates in both directions from the point at which transition occurs.

(iii) With charges of intermediate size, i.e., 50 mm square cross-section by 150 mm long, there is an intensification of the shock over a distance of about 10 - 15 mm; detonation waves propagate in both directions but the propagation in the direction counter to the initial shock, and in the region over which intensification has taken place, is confined to the corners of the charge and may be inhibited on one side by the removal of the corners in the region and on that side.

It is concluded that the transition from shock to detonation is by a continuous build-up process, and that this proceeds faster in the centre of the charge than in the outside layers. The effect of the continuous nature of the build-up is that the region immediately behind the point of transition to detonation is devoid of chemical energy and does not permit propagation. If however this process proceeds faster in the centre than at the sides, given a charge of sufficient cross-section there will be zones of unreacted material which will propagate detonation back from the transition point towards the face through which the initial shock wave entered. All experiments were recorded by high-speed photography and a film of the most important experiments has been made.

Detonation Plasma

As a minor part of the general investigation of the initiation of high explosives by shock, a study has been made of the luminosity generated by a detonating explosive. This has been variously described as "luminious air shock", "shock waves reflected into the detonation products" or "plasma ejected by the detonation zone".

The following experimental methods have been used:

(i) Explosive charges have been fired in atmospheres of air, carbon dioxide, propane and neon.

(ii) The "plasma" produced by a charge fired in air has been made to enter an atmosphere of carbon dioxide, propane or neon.

/(iii) .....

(iii) The effect has been photographed in a Schlieren field.

(iv) Charges have been fired in vacuo, in some cases in contact with a steel block.

In all cases records were made in colour with a high-speed camera working at 1,200,000 frames per second.

The nature of the light emitted was found to be controlled by the atmosphere; in air a lilac colour was seen which changed to pink in neon or was masked by a black cloud in propane or carbon dioxide. The light is emitted by a region in contact with the outside surface of the explosive products and cannot be separated from the air shock, which, very close to the charge, is also near to the products. The light is completely suppressed by evacuation of the charge to 5×10^{-5} mm Hg, with the exception of a zone in contact with the steel block.

It is concluded that gas surrounding the charge has been brought to a highly ionised state by shock compression. The production of light by the reflection of a shock into the explosion products had also been demonstrated, but this can only be effective if the shock impedance of the products is lower than that of the material in contact with it, a condition usually met with only if this material is a solid.

A film illustrating the more important features of the investigation is being prepared.

XXVI.3 EXPLOSIVE HAZARDS

Detonability of High-Impulse Cordite Dough (Solvent Process)

A series of trials has been carried out, at E.R.D.E. and at P. & E.E. Shoeburyness, to investigate hazards in several alternative methods of manufacturing high-impulse cordite by the solvent process. Materials from different stages of manufacture were ignited, in containers of different shapes and sizes, by a "puffer" (Fuze, electric, F.53), alone, or with primed cambric. The means of ignition was always placed at the bottom of the container. The size of container ranged from 6-inch cubical tins containing from 1 to 4 lb of material to incorporator replicas $28\frac{1}{2}$ x 31 x 31 inches deep, containing 180 or 300 lb of material.

The propellant on which the trials were made was cordite F.452/271. Details of the composition and of the solvent contents are given in Table 5 overleaf.

/TABLE 5 .....

TABLE 5

Details of Compositions

Percentage of Constituents	Composition Number (Cordite F.452/271 Used):				
	1	2	3	4	5
Aluminium (atomised)	23.2	23.2	39.5	23.2	23.2
Ammonium perchlorate	35.0	35.0	59.7	35.0	35.0
Pyro N.C. (12.6% nitrogen)	31.3	31.3	-	31.3	31.3
N.G.	10.0	10.0	-	10.0	10.0
2-N.D.P.A.	0.5	0.5	0.8	0.5	0.5
Acetone	-	20	20	-	-
Ether	36	-	-	-	-
Alcohol	24	-	-	8.75	24

Notes:

Composition 1 is the final bound product using 60% ether/alcohol (60:40) solvent

Composition 2 " " " " " " 22% acetone solvent

Composition 3 is an intermediate stage in the process using 22% acetone solvent

Composition 4 is the pre-final stage product in the process using 25% alcohol/acetone (35:65) solvent

Composition 5 is the pre-final stage product in the process using 60% alcohol/ether (40:60) solvent.

It was found that Composition 4, which had a low solvent content, was the only one tested which burnt to detonation as a result of ignition by a puffer alone or by a puffer plus primed cambric.

The results are considered to be applicable only to the propellant tested and only for the particular conditions of test employed. Major factors in assessing, by comparison, the risk with other propellants would be solvent content and the available energy of explosion.

/Electrostatic .....

Electrostatic Hazards: Resistances of Conductive Rubber and P.V.C. Samples and Flooring

The variations in resistance of samples of conductive rubber with applied voltage have been studied systematically. Using the wet electrodes recommended in BS.2050: 1958, nearly all the resistances were reduced by a factor of 2 or 3 for a six or sevenfold increase in test voltage.

Resistance measurements to earth on one conductive and two antistatic floors in E.R.D.E. have been made using both wet and dry test electrodes, and applied voltages from 15 to 500 volts. The values obtained with the wet electrode followed more closely those obtained when a person wearing conducting footwear stands on the floor, although there was no exact equivalence. The values obtained on the respective floors correlated reasonably well with actual electrostatic potentials acquired in vigorous foot movements on these floors.

The lower test voltages showed higher resistance values just as with the small samples. Since lead azide, especially, can be ignited by discharges between metal electrodes at much lower voltages than 500 volts, e.g. 90 volts for a capacitance of 500 $\mu\mu F$, resistance tests on antistatic systems should therefore be carried out at a lower test voltage. The only established test which fulfils this condition is the Personnel Test Meter used in the R.O.F.s. This uses an applied test potential of 80 volts, when the maximum resistance between the hand electrode and earth indicating "SAFE" is one megohm. A report of this work (E.R.D.E. 22/R/60) is being prepared.

Electrostatic Hazards with Polythene

With the proposed extensive introduction of polythene for packaging purposes, electrostatic charges have been measured in attempts to assess the hazard to the explosive stores concerned. With a view to establishing an antistatic polythene samples of massive polythene loaded with carbon black (supplied by S.R.O.F. Woolwich and S.M.R./E.R.D.E.) have been tested. So far, the only products found satisfactory are ones produced by compression moulding.

In the case of flexible sheet polythene, an antistatic grade of material considerably reduces the hazard under normal conditions, but is not satisfactory if exposed to extremely dry or wet climatic conditions.

XXVI.4 EVALUATION OF THE SENSITIVENESS OF INITIATORS

Impact Sensitiveness of Initiators

A series of trials has been carried out to determine whether the probability of ignition of mercury fulminate can be correlated with the kinetic energy or the momentum of the drift used to impart the blow in the ball and disc impact machine. In order to do this, a wide range of drift masses and ball masses has been used, with an "up and down" technique for 50 per cent probability of ignition. The results show that, except for small drift masses, the momentum of the drift for 50 per cent probability of ignition is directly proportional to the drift mass. A less detailed series of trials carried out with Service lead azide supports this conclusion.

/Estimates .....

Estimates of impulsive pressures have required a study of the variation of the energy and momentum with the area of the impacting surface. A series of trials has been carried out with drifts containing a range of flat-ended punches, since the impacting area of a spherically ended drift, i.e., the normal drift of the ball and disc machine, is not easy to determine. The results show that the previously accepted relationship of direct proportionality between energy and impact area is not obeyed. In fact the height of fall of the ball is proportional to the radius of the impacting punch raised to a power between 3 and 4. The exact relation awaits measurements of the impact time and their comparison with theoretical values. These results are compatible with the requirement of a constant impulsive pressure for ignition as the impacting area is changed.

/XXVII .....

XXVII CHEMISTRY OF PROPELLANT INGREDIENTS

XXVII.1 NITROCELLULOSE

Fractionation of Nitrocellulose

Examination of the nitrocellulose from the propellant of the French S.S.11 weapon has been completed by the fractionation of the ether/alcohol soluble and insoluble portions in the original and renitrated conditions. The results support the suggestion previously made, that the original nitrocellulose is a blend of a low-viscosity, fairly high nitrogen and a high-viscosity, low nitrogen material. In the course of this work it has been found that the separation from solutions of precipitated fractions, which is often slow and incomplete, can be greatly improved by the preliminary addition of about 3 per cent of water to the acetone solution when hexane is used as precipitant, and of about 4 per cent of carbon tetrachloride when water is used.

It has recently been suggested by Onyon (Nature, June 13, 1959) that the ratio of the viscosity-average molecular weights of a polymer sample, as determined in a "good" and a "poor" solvent, could be used to classify the molecular weight distribution. Some experiments have been carried out to determine whether it is possible to simplify this approach by using the ratio of the intrinsic viscosities of nitrocellulose in a good and a poor solvent (butyl acetate and 90/10 acetone/hexane) and so dispensing with the necessity for knowing the values of the constants for the two solvents in the Mark-Houwink equation, on which Onyon's treatment is based. The value of the ratio for a laboratory-prepared sample of nitrogen content 12.5 per cent, was found to be 1.323, while a number of fractions derived from it gave values varying from about 1.2 to 1.3. The original material from the S.S.11 gave a value of 1.337 which suggests a higher degree of polydispersity than that of the laboratory sample. Fractionation of a sample prepared by renitration of Bishopton guncotton to 14 per cent nitrogen gave fractions with ratios varying from about 1.18 to 1.27 (except for a "head" fraction with a ratio of 1.35), that for the unfractionated sample being 1.364. Characterisation of the fractions by refractionation showed that, although they were less heterogeneous than the original material (i.e., their distribution curves were smoother), the intrinsic viscosity ranges covered varied from 12.5 - 2.5 in the highest D.P. sample to 1.5 - 0.25 in the lowest D.P. sample. This variation in range was not reflected in the ratio of intrinsic viscosities.

The ratio of intrinsic viscosities in the two solvents for mixtures of nitrocellulose has been found to be always higher than the mean calculated from the ratios for the constituent nitrocelluloses and their proportions in mixture.

Reaction between Nitrocellulose and Lead Compounds in Solution

Examination of the nitrocellulose referred to in QTR.3/59, was continued on the lines described there. For lead 2-ethylhexoate in acetone solution the following results were obtained:

(i) None of the solutions gave a firm gel, even when higher concentrations of nitrocellulose were used to give initial viscosities up to 1000 centipoises.

(ii) Partial gel-separation occurred in some solutions and the lead concentration corresponding with the "maximum viscosity" (obtained by extrapolating the portions of the lead concentration/viscosity curve on either side of the

/gelling .....

gelling range) falls into a continuous relationship with those for non-gelling solutions. Thus, the point of maximum viscosity in non-gelable solutions does not correspond with the onset of gelling (c.f. QTR.3/59).

(iii) For each nitrocellulose in a series of solutions, the ratio of lead salt concentration to nitrocellulose concentration giving rise to the maximum viscosity falls as the nitrocellulose concentration increases.

(iv) At the same level of nitration and original solution viscosity, the maximum viscosity is produced at the lower lead concentrations and the higher the average D.P.

(v) At the same average D.P. and original solution viscosity, the maximum viscosity is produced at the lower lead concentrations the higher the nitration level.

(vi) The lead concentration required to produce the maximum viscosity is in all cases less than one-fifth (and in some instances as little as one-twentyfifth) of the free hydroxyl equivalent (regarded as one atom of lead for two hydroxyl groups). The cloudiness that appears in the solution at some stage beyond the maximum viscosity point, earlier thought to represent completion of the interaction, corresponds with less than two-fifths of the free hydroxyl equivalent.

(vii) Increase of lead concentration beyond the "cloudy point" produced further lowering of viscosity, and values below the initial (no Pb) value are ultimately reached. This observation has been repeated in actual solvents. In the only case followed through, in acetone solution a minimum viscosity point was found at a lead concentration in the region of full hydroxyl equivalence, with a rise of viscosity at higher lead concentrations.

(viii) Mixing portions of a nitrocellulose solution to which different concentrations of lead (or none) have been added results in solutions with viscosities close to those predicted from the lead concentration/viscosity curve even when this involves a return to a higher viscosity; when the cloudy-point has been passed the precipitate may dissolve.

The failure of these materials to give firm gels is in contrast with the behaviour of factory-made samples (12.2 per cent nitrogen wood and cotton, and 13.1 per cent cotton of two viscosities) used in earlier experiments, which gave rigid gels at initial viscosities as low as 1.5 per cent. These experiments were carried out on samples de-ashed by acid washing; the present materials had been alcohol-stabilised and not acid-washed. However, only small variations in the position of the maximum viscosity point were found when samples of the same crude nitrocellulose made from linters of the appropriate D.P. were alcohol or water-stabilised and used in the acid-washed or non-acid-washed condition, and none of these materials gave firm gels. The maximum viscosity points for all these samples were at a considerably higher level than those for acid-washed and non-acid-washed Caerwent 12.2 per cent nitrogen material. This difference is still being investigated.

Extension of the investigation to other solvents has shown that a similar type of viscosity/lead-content relationship exists for nearly all of those used, but the maximum viscosity for solutions of the same nitrocellulose concentration occurs at widely different lead concentrations and the viscosity increase is small in some cases. Diethylene glycol and 1:1 D.E.G./D.E.G.N. solutions showed only a <u>fall</u> in viscosity on addition of lead salt. The type of behaviour, and the position of the maximum viscosity point, thus vary with the solvent/polymer

/interaction .....

interaction; and while the free hydroxyl content of the nitrocellulose is of importance there is no apparent stoichiometrical relationship.

Attempts have been made to follow the interaction conductimetrically and potentiometrically. Curves with sharply defined minima were obtained for conductivity against lead content but it has not been possible to interpret these as representing any quantitative relationship.

Analysis of the white precipitate formed in solutions beyond the "cloudy point" has shown this material to have the same lead content as that formed in acetone solutions of lead ethylhexoate. This corresponds very closely to a simple basic lead ethylhexoate, and presumably the white solid owes its origin to the action of traces of water.

Reaction between Nitrocellulose and Ammonium Perchlorate

Work has been started on this topic. The first experiments, involving the heating of equal weights of nitrocellulose and ammonium perchlorate in acetone at 40°C in the presence and absence of water and under slightly acid and alkaline, as well as "neutral", conditions, are not yet complete but it is clear that, ceteris paribus, the presence of the perchlorate increases the rate of degradation of the nitrocellulose.

XXVII.2 BORANES

The study of the kinetics of the formation of pentaborane from diborane has been concluded and a report written.

A research programme has been initiated into high temperature reactions of decaborane.

The pyrolysis of decaborane has been investigated in sealed glass reaction vessels in the temperature range 210° - 250°C. Analysis of the unreacted decaborane and the products indicate that in the initial reaction one molecule of hydrogen is formed from one molecule of decaborane, i.e:

$$B_{10}H_{14} \rightarrow H_2 + \text{solid products.}$$

The rate of decomposition of decaborane has been shown to be first order, slightly retarded by hydrogen, with an activation energy of 41.6 kcal/mole. Hydrogen has also been shown to retard the formation of hydrogen from nonvolatile solid hydride. The following mechanism has been proposed and shown to account for the experimental facts.

$$B_{10}H_{14} + B_{10}H_{14} \rightleftharpoons B_{10}H_{14}^{*} + B_{10}H_{14} \quad \text{..........} \quad 14$$

$$B_{10}H_{14}^{*} \rightleftharpoons B_{10}H_{12} + H_2 \quad \text{..........} \quad 15$$

$$B_{10}H_{14} \rightleftharpoons \tfrac{1}{2} B_{20}H_{24}(S) + H_2 \quad \text{..........} \quad 16$$

$$B_{20}H_{24}(S) \rightleftharpoons \text{polymer} + H_2 \quad \text{..........} \quad 17$$

/The .....

The slow steps are given by equations 15 and 17.

Attempts have been made to react decaborane with alkylating agents in the presence and absence of catalysts. It was found that methane, ethane and ethylene did not react with decaborane to form ethyl decaborane. However, ethyl bromide and decaborane form ethyl decaborane at 230°C, the yield being consistent with the view that the decaborane radicals are the active species in the reaction. In the presence of aluminium chloride the reaction rate is considerably increased, and this is now being studied; in contrast to the results of alkylation in solution at lower temperatures, the present work has yielded monoethyl decaborane as the only alkylated product isolated. The best result to date was obtained using equimolar quantities of reagents, reaction time 5 min, when 25 per cent of the decaborane was converted to ethyl decaborane, 16 per cent to nonvolatile solid hydrides and the remainder(59 per cent) recovered unchanged.

Alkylation of Boron Hydrides

The reaction of decaborane with Grignard reagents to give decaborane monomagnesium iodide has been further examined. Formation of 5-alkyl derivatives from the decaborane Grignard reagent and various alkylating agents was reported in QTR.3/59; 6-methyldecaborane was obtained as a by-product in each case. Decaborane monomagnesium iodide was prepared by treating decaborane with ethyl magnesium iodide, instead of with methyl magnesium iodide as previously; the product when treated with dimethyl sulphate yielded 5- and 6-methyldecaborane and 6-ethyldecaborane; unreacted decaborane was present and some disubstitution occurred.

A Friedel-Crafts methylation of decaborane has been performed in a glass-lined stainless steel autoclave. The product was separated into mono- and polymethylated derivatives of decaborane by preparative gas chromatography and the components were characterised by retention volume data, infra-red and n.m.r. spectroscopy and elemental analysis; the melting-point of each compound was determined.

Boron-Nitrogen Compounds

Some displacement reactions of bisacetonitrile decaborane, $B_{10}H_{12}(CH_3CN)_2$, have been studied. Hydrazine reacted with bisacetonitrile decaborane to give the hydrazinate of bisammonia decaborane, $B_{10}H_{12}(NH_3)_2.N_2H_4$. Attempts to convert this compound to bisammonia decaborane, $B_{10}H_{12}(NH_3)_2$, by heating at 120°C under diminished pressure (10 mm Hg), were not successful; almost quantitative conversion occurred when the material was recrystallised from hot water. Synthesis of bisammonia decaborane by the direct action of ammonia on decaborane is being examined.

The yellow, high-melting-point solids formed by the action of redistilled triethylamine on decaborane and bisacetonitrile decaborane were investigated. Decaborane reacts with triethylamine to yield a covalent compound, $B_{10}H_{12}(NEt_3)_2$, and an isomeric compound which exhibits ionic properties and is insoluble in benzene.

/Carborane .....

Carborane Chemistry

Various carborane derivatives (general formula, $B_{10}H_{10}.C_2RR'$) have been prepared by treating benzene solutions of decaborane with diethyl sulphide and substituted acetylenes. Carborane ($B_{10}H_{10}.C_2H_2$) has been obtained by alkaline permanganate oxidation of 11,12-bis-acetoxymethyl carborane.

Optimum conditions for the synthesis of these compounds are being investigated. Reaction between decaborane and an acetylenic derivative requires the presence of a Lewis base containing a Group V or Group VI element (for example, a nitrile, sulphide, or ether). The reaction of such electron donors with decaborane is being studied kinetically and the research will be extended to reactions involving decaborane, Lewis base and substituted acetylene.

Properties of Boranes and Alkylboranes

Hydrolysis of decaborane and its alkyl derivatives has been studied kinetically with particular regard to the mechanism of the reaction.

The rate of hydrolysis of decaborane in dioxane/water and in dioxane/aqueous normal hydrochloric acid at 30° and 35°C has been determined by measuring the evolution of hydrogen:

$$B_{10}H_{14} + 30\ H_2O \rightarrow 10\ B(OH)_3 + 22\ H_2$$

The initial slopes of curves relating hydrogen evolution to time suggest that the early stage of hydrolysis is a second order reaction having activation energies of 17.7 and 22.2 kcal/mole in neutral and acid media respectively.

A smooth curve relating hydrogen evolution to time was obtained when the hydrolysis was performed in aqueous dioxane at 30°C. However, in the presence of dilute mineral acid, the initial rate of hydrolysis was markedly increased and the curve exhibited breaks corresponding to approximately 20 and 55 per cent hydrolysis; beyond the second break in the curve, reaction was very slow. A likely explanation of the shape of the hydrolysis curve may be initial rapid attack at bridge positions, catalysed by acid, followed by a slower reaction in which B-B and B-H terminal bonds are hydrolysed.

2-Ethyldecaborane behaved in a similar manner on hydrolysis; activation energies in neutral and acid media were 14.9 and 17.3 kcal/mole respectively.

The relative initial rates of hydrolysis of decaborane, 2-, 5-, and 6-ethyldecaborane, and 2-, 5-, and 6-methyldecaborane have been compared at 30°C in a dioxane/aqueous normal hydrochloric acid medium. The alkyl-substituted derivatives are all more stable to hydrolysis than decaborane, their order being 6>5>2, with no significant difference between the effects of corresponding ethyl and methyl groups. Hydrolytic stability of alkylboranes increases with the number of alkyl substituents in the molecule.

Iodo derivatives of decaborane are hydrolysed more easily than is the parent borane.

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XXVIII CHEMISTRY OF HIGH EXPLOSIVES

XXVIII.2 TNT

Dark RDX/TNT

When RDX (Grade I, recrystallized from cyclohexanone by steam-distillation of the solvent) and TNT (Grade I) are incorporated at temperatures of 100° - 115°C the resultant mixture varies in colour from a pale fawn to a chocolate brown. The RDX is nominally white, but may be buff coloured; the TNT is light brown; the product is much darker than the starting materials. There is obviously a reaction proceeding during the incorporation which results in a dark coloured constituent. The users of RDX/TNT condemn the dark colour, and hence it is desirable to know the method of its formation so that it may be minimized. A related problem is the occasional occurrence of badly discoloured RDX with a rancid odour when the recrystallization from cyclohexanone is carried out more slowly than usual.

While the possibility of reaction between RDX and TNT must not be excluded, it seems probable that the occluded cyclohexanone and nitric acid in the RDX are the primary causes of colour formation. Experiments have shown that brown colours are produced by heating cyclohexanone alone, cyclohexanone and RDX, cyclohexanone and TNT, cyclohexanone and nitric acid, and cyclohexanone and ammonium nitrate. Chromatography has shown that the products of the last two reactions are mixtures of many compounds.

The progress of these reactions was followed by either ultraviolet absorption (using a Unicam SP 500) or by visual colorimetry (using a Klett comparimeter with a set of arbitrary colour standards). The results have given information about the relative rates of the reactions involved, but it is not yet possible to deduce reaction orders or rate constants. So far not much is known about the mechanisms of the reactions involved, but the following conclusions relative to the main problem have been drawn:

(i) When cyclohexanone is heated, alone or with cyclohexanol, at 96°C, a series of reactions leading to brown coloured products take place. The sequence of the reactions involved depends upon the amount of cyclohexanol present. (The cyclohexanone used at Bridgwater contains 10 - 15 per cent cyclohexanol). The rate of colour formation is relatively slow, and it is unlikely that such reactions make much contribution to the colour of dark RDX/TNT. There is a possibility that the condensation products react with other constituents of the RDX/TNT mixture to give deeply coloured products.

(ii) When RDX (Bridgwater Grade I) is heated with cyclohexanone at 96°C brown coloured products are formed. The nature and extent of the reaction are modified by the presence of cyclohexanol. This reaction is relatively slow, and is only likely to lead to colour trouble when there is prolonged contact at high temperatures between RDX and cyclohexanone.

(iii) When purified TNT is heated at 96°C with cyclohexanone very dark brown products are formed. (For this and the following experiments the cyclohexanone contained 4 per cent cyclohexanone). When cyclohexanone alone is used as the reaction medium, with low TNT concentrations, the rate of reaction is independent of the TNT concentration. This is also true when using chlorbenzene as a medium with low concentrations of cyclohexanone in 1 to 4 moles

/excess .....

excess over the TNT. The rate of reaction is, however, ten times greater in cyclohexanone than in chlorbenzene. Reactions in cyclohexanone/chlorbenzene mixtures have an initial inhibitory period. Under certain conditions these reactions can be very fast, and could lead to the appearance of dark colours in RDX/TNT.

(iv) Cyclohexanone reacts with traces of dilute nitric acid at 96°C to give brown coloured products. This reaction is much faster than any of the foregoing, and the rate is proportional to the square of the nitric acid concentration. This reaction is a very likely source of the colour in dark RDX/TNT. Its existence precludes the idea of using an increased nitric acid content in Grade I RDX to diminish any possible "indicator" colour in TNT.

(v) Dilute acetic acid has no marked effect on reactions leading to colour formation in cyclohexanone at 96°C. This observation is of interest with regard to the lighter coloured RDX/TNT obtained using RDX(B).

(vi) It was hoped that addition of ammonium acetate would buffer the nitric acid and thus reduce its effect on colour formation in cyclohexanone at 96°C. It actually increased the rate of colour formation, and broadened the absorption bands of the coloured products. This enhancing effect was diminished as the ratio $[NH_4OAc]/[HNO_3]$ was increased. It thus seems possible that buffering may partially suppress colour formation, but that the ammonium ion has a specific deleterious effect.

(vii) Cyclohexanone reacts with traces of dilute aqueous ammonium nitrate at 96°C to give brown coloured products. This reaction is a fast one, and the rate is proportional to the ammonium nitrate concentration; it could give rise to the colour in dark RDX/TNT.

(viii) The last four conclusions are consistent with the development of colour being due to the presence of cyclohexanone and nitric acid, the rate of development being mainly proportional to the concentration of the latter.

Pick-up Sensitive RDX/TNT

Although laboratory scale recrystallizations at E.R.D.E. have consistently given RDX with the desired response to shock-initiation, the few full-scale runs made at R.O.F., Bridgwater have not proved satisfactory. Advice on steps to improve the plant conditions has been given; pending completion of the modifications, the laboratory work has been continued with regard to tolerances on some of the controllable conditions of operation.

Two series of experiments have been made in which rates of distillation were varied rather widely, one series being confined to indirect heating through the vessel wall (glass) below the level of the liquid surface, the other series involving heating by injection of live steam. In all cases, products of satisfactory gap-test value were obtained; the differences attributable to the controlled variations in procedure were too small to be considered significant.

Variations in the ratio of HMX to RDX and in the amount of RDX recrystallization during the run have been made, all the HMX being present in the still from the start. Under these conditions, satisfactory sensitiveness results have been obtained with as little as 0.125 per cent of HMX. Larger quantities of HMX did not give consistently or notably increased shock-sensitiveness.

/After .....

After-treatment of the product by prolongation of refluxing for three or six hours after completing the addition of RDX solution, or by temperature-cycling for some hours between 40°C and the boiling point (67.5°C), has been found to reduce slightly the gap test sensitiveness.

Preparations under otherwise normal conditions, but with the stirrer speed reduced to one-half and one-quarter respectively of the normal, gave products with sensitiveness below the acceptable level.

XXVIII.3 OTHER EXPLOSIVES

Spray Crystallization of Mixtures

The technique of preparing mixtures by spray crystallization of a mixed slurry through a jet has been explored further - (a) as a general method, (b) as applied to composite propellant ingredients, and (c) as applied to pyrotechnic and igniter composition ingredients.

As a general method, aluminium powder, representing an insoluble constituent, has been mixed with a number of soluble salts giving a range of solubility differences from 8 g. to 52 g/100 g. water, expressed as the difference in solubilities between saturation and final spraying temperatures. By this means the effectiveness of incorporation of aluminium powder has been related to solubility difference and the particle size of the powder.

For propellant applications, batches up to 20 lb ammonium perchlorate containing 18 per cent aluminium powder and minor constituents (catalysts) have been made in spraying runs at the rate of 5 to 6 lb per hour.

For use in the preparation of igniter compositions, Types IT.7 and IT.10, potassium perchlorate has been spray-crystallized with boron and a small proportion of carbon black or semi-colloidal graphite. Preliminary results are promising, indicating that good mixing, curing and burning resulted from the use of the spray-crystallized mixture. Following discussions with A.R.D.E.(X4) a number of spray-crystallized mixtures have been prepared for pyrotechnic requirements, including S.R.812 (potassium perchlorate/aluminium), SR.53 (boron/silicon/potassium dichromate), S.R.580 (magnesium/acaroid resin/sodium nitrate). These experimental products are being examined for sensitiveness and functioning in order to make an assessment of manufacturing, safety and Service features, in comparison with existing mechanical mixtures.

Miscellaneous Preparations

Preparations of the following materials have been completed during the period:

ε-Caprolactone (2 kg),
Methoxymethyluron (1 kg),
Unsymmetrical dimethylhydrazine (2.5 grams),
2-methyl-5-vinyl tetrazole (200 grams),
Lead trihydroxyglutarate (500 grams).

A small quantity of β,β,β',β'-tetranitrodipropylene glycol has been prepared by the route indicated. This material is of interest as of possible use for the preparation of polyesters containing nitrogroups:

/Formulae .....

$$(ICH_2CH_2)_2O \xrightarrow{AgNO_2} (NO_2CH_2CH_2)_2O \xrightarrow[HCHO]{NaOH}$$

$$(CH_2OH.CHNO_2CH_2)_2O \xrightarrow[NaNO_2]{AgNO_3} (CH_2OH.C(NO_2)_2.CH_2)_2O$$

The viscosities of D.E.G.N. and T.E.G.N. and the density of the latter have been measured at three temperatures. The values obtained are:

TABLE 6

t:	25°C	40°C	60°C
D.E.G.N. μ_t (cS)	2.7265	1.8244	1.3235
T.E.G.N. (μ_t (cS)	4.6078	2.8187	1.9168
(d_t	1.3177	1.3004	1.2778

/XXIX ......

XXIX CHEMISTRY OF INITIATORS

XXIX.1 L.D.N.R. and Other Lead and Barium Salts of Nitrophenols

Barium Styphnate

The preparation and properties of the hydrates and polymorphic modifications of barium styphnate are being studied with regard to suitability for high temperature uses and for electric initiation applications. The identities and characteristics of these substances have now been clarified. Thus Type 1, the common polymorph of the monohydrate, is stable up to 210°C but the presence of any of the other types lowers the temperature of decomposition substantially. Type II, which appears to have been erroneously described both as an anhydrous salt and a monohydrate, is proved to be a $1\frac{1}{2}$ molecular hydrate. It decomposes at 140°C and, somewhat surprisingly, it is converted to the monohydrate on treatment with water; its stability in water can be influenced by its method of preparation. Type III is confirmed as a true polymorphic modification of Type I, i.e., monohydrate. It has been prepared only in the presence of certain types of polyvinyl alcohol. It is quite stable but thermal decomposition begins at 150°C, i.e., lower than the Type I polymorph. On dehydration Types I and III give different anhydrous salts; in this respect the behaviour of barium styphnate resembles that of lead styphnate.

Lead Styphnate

Variation in the particle size of Composition R.D.1303 manufactured on the Woolwich plant has been traced to the transient formation of the unstable beta polymorph during the early stages of crystallization. Possible means of suppressing this polymorph have been investigated and a promising solution is the addition of a small proportion of polyvinyl alcohol. Results of trial runs indicate both elimination of beta lead styphnate and improvement in regularity of the product. Sensitiveness and functioning tests are in progress.

Monobasic lead styphnate of the modified beta type (R.D.1349) has been prepared on the plant scale ($4\frac{1}{2}$ lb) and supplied to Messrs I.C.I. Ltd. for tests as a fusehead composition. The results are very promising for both pasting and sensitivity requirements. This form of lead styphnate has now shown to be unchanged at temperatures up to 200°C and is of special interest for applications where stability above 100°C is important.

XXIX.3 OTHER MATERIALS FOR INITIATOR COMPOSITIONS

Tetrazene

The preparation and properties of this explosive have now been studied extensively with particular reference to the formation and stability of A and B types and optimum conditions of manufacture for the new granulated composition R.D.1357. It has been shown that the appearance of either A or B types during crystallization is determined largely by temperature conditions. Thus by restricting the process temperature to 60°C the A type is suppressed and highest yield obtained giving a batch size of 2 lb 10 oz. The same product has also been prepared by a continuous process.

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The stability of tetrazene and tetrazene/lead styphnate mixtures has been examined and advice given to S.R.O.F., Chorley in connection with the operation of cap composition plants. Ordnance Board and other trials are now in hand covering the substitution of R.D.1357 for commercial tetrazene in both cap and detonating compositions. The advantages sought are those of convenience and safety in handling; moreover, the former product is properly specified and not liable to vary in quality.

Lead Azotetrazole

The basic lead salt is of potential application as the primary dip for very sensitive fuseheads. Two difficulties have been encountered - the sensitive C type is unstable on storage under water, and occasionally cavities have occurred in the fusehead bead, resulting in some loss of sensitivity in functioning. It is believed that the first difficulty has been overcome by the crystallization of the stable D type in the presence of an additive; results from Messrs. I.C.I. Ltd. indicate successful substitution. The second difficulty still persists although improvement has been obtained by the addition of a small propertion of L.M.N.R. to the paste and by later modifications of the D type crystal size and shape.

Information for Other Countries

Information and advice has been given to various authorities abroad including Picatinny Arsenal (lead azides R.D.1333, R.D.1343, R.D.1352, tetrazene R.D.1357, lead styphnate R.D.1303, silver azotetrazole and modified potassium picrate). A recent review of lead azides by Picatinny Arsenal recommends that R.D.1333 should be used in all new detonator design work (Technical Report No. 2662,1960). Canadian Arsenals have been advised on the manufacture of lead styphnate and the Australian Department of Supply on lead azide R.D.1352, tetrazene and dinitroresorcinol.

/XXXI .....

XXXI CHEMICAL ENGINEERING

XXXI.1 RESEARCH

XXXI.1.1 Heat Transfer

The Thermal Conductivity of Kerosine D. Eng. R.D.2495

The thermal conductivity of Aviation Kerosine, Specification No. D.Eng. R.D.2495, has been measured with a vertical, co-axial cylinder apparatus in the temperature range 15° to 325°C at pressures between 1 and 200 atm. The trend of the results, demonstrated by the influence of temperature and pressure on the thermal conductivity, is characteristic of normal, non-associating liquids. The experimental values were tabulated, and smoothed graphs, showing the variation of thermal conductivity with temperature and pressure, have been prepared. The effect of pressure on the thermal conductivity, expressed in terms of the pressure coefficient $(1/k_o)(\partial k/\partial P)_t$, is considerably higher than that for heavy water, which had been studied previously. It is believed that the high pressure coefficient of kerosine is related to the higher compressibility of paraffins, compared with water.

At temperatures in excess of 280°C noticeable thermal decomposition of kerosine took place, believed to be due to the catalytic effect of the material of the receiving cylinder, a 97/3 per cent copper-nickel alloy. About 4 per cent of toluene, a substance absent in the original sample, was detected after this kerosine had been exposed for about 7 days to temperatures between 280° and 320°C (approximately the same figure as the content of aromatic and olefinic hydrocarbons present in the original sample). After replacing the receiving cylinder with one of solid silver no decomposition took place within the same temperature interval, and it was possible to conclude the measurements with normal results. This investigation has been completed, and a report is in preparation

The Thermal Conductivity of Anhydrous Ammonia

Despite its importance as a basic material in many chemical processes the thermal conductivity of anhydrous ammonia in its liquid state, and in the gaseous state at high pressures, has not been reported before. Experimental studies on this substance commenced this year and the work completed so far ranges from 15° to 125°C and from 1 to 140 atm. pressure. This work broadly confirms an earlier general statement by Kardos, according to whom the thermal conductivity of ammonia is of the same order as that of water.

Measurements are being continued to study the effect of pressure up to 500 atm and to extend the temperature range well beyond the critical temperature (132.4°C).

The Thermal Conductivity of Toluene

In view of the experimental difficulties connected with an absolute determination of the thermal conductivity of a liquid, preference has often been given to relative methods which presuppose knowledge of the thermal conductivity of a suitable calibrating fluid. With the exception of water there is hardly a liquid of which the thermal conductivity has been determined by several observers with satisfactory accuracy.

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For several reasons water is not an ideal substance as a calibrating liquid, and to satisfy a long-felt demand for a more suitable substance, the thermal conductivity of toluene has been studied from about -15° to 110°C. These results were compared with reliable earlier measurements and, by a careful analysis of all these data, an equation was derived which predicts the thermal conductivity of toluene with an accuracy of better than 1 per cent between the above temperatures, and probably within 2 per cent between -80° and -20°C. A report on this investigation is being prepared.

Heat Transfer in Cylindrical Combustion Chambers

The object of this investigation is to study the influence of aerodynamic phenomena on convective heat transfer, in particular, of Reynolds' number on the enhancement of the local convective heat flux.

A multi-section chamber assembly was used, consisting of six sections 0.5 inch wide, and five sections 1 inch wide, all of 1.5 inches diameter. Gaseous hydrogen and gaseous oxygen were used as the propellant system and all tests were conducted at 10 atm. combustion pressure. Although the analysis of the results is still incomplete, some significant facts have emerged from a preliminary evaluation:

(a) The local heat flux in the first 0.5-inch section immediately downstream of the injector is practically independent of mass flux within the range studied, i.e. from 4 to 24 g/cm^2s. It is extremely high and amounts to about 350 cal/cm^2s.

(b) For mass fluxes below 12 g/cm^2s. there is a steep and continuous fall of the local heat flux with increasing distance from the injector. For values of mass flux 12 g/cm^2s. and higher, there is a similar steep fall up to a distance of about 0.9 D (where D is the diameter of the chamber), followed by a rise with further increasing distance. A maximum of local heat flux is reached at about 1.6 D, followed by a further continuous fall.

(c) For distances greater than 3.5 D, the local heat flux values, after an appropriate deduction for radiation, are proportional to the 0.8 power of the mass flux.

It is concluded that, at all mass fluxes, combustion takes place at the injector face; the zone of highest temperature coincides with the zone of undeveloped flow boundary, hence the high values of heat flux observed. At the higher mass fluxes (12 g/cm^2s. and above) the boundary layer appears to detach itself from the wall and thus causes a rise in heat flux after the initial drop up to distance of about 0.9 D. Re-attachment follows at a distance between 0.9 D and 2 D. This phenomenon has been observed by other workers studying the effect of undeveloped flow on heat transfer in cylindrical ducts. The last-mentioned observation, viz the proportionality between a power of the mass flux and the convective heat flux, confirms an assumption made earlier in connection with tests on the radiative and convective heat transfer in rocket combustion chambers.

XXXI.1.2 Crystallization

Continuous Crystallization of Barium Nitrate

The barium nitrate crystals made in the elutriator-crystalliser were submitted to A.R.D.E. and found to be suitable for initiator compositions. D.O.F.(F) have therefore been advised to use this process and have been given details of the apparatus so that a unit could be installed at R.O.F., Glascoed.

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Work continues, however, on the analysis and control of performance of the system. Some modifications were incorporated in the final design, including a "mono" pump instead of a centrifugal pump feeding the elutriator. It was expected that this would reduce crystal breakage, but no effect on crystal size was found. An experiment in which circulation outside the crystallizing vessel was stopped gave much larger crystals, and it appears therefore that some nucleation or crystal breakage occurs in the recirculating system. In order to permit a quantitative examination of the performance of the apparatus the rate of growth of barium nitrate has now been measured in the dipping refractometer cell at 25°C on 170 mesh crystal. The linear growth rate for 95 micron crystals was found to be 3.1 microns per minute per 1 per cent supersaturation. Careful checks on the solubility at 25°C of barium nitrate crystals of three extremes of physical state were made, with an accuracy of 1 in 10,000. The results indicated a variation of 1 in 300 in the equilibrium concentration. The figures obtained were 10.12, 10.11, and 10.14 g. $Ba(NO_3)_2$/100 g. H_2O at 25°C, the last being for milled crystals. By approaching equilibrium from a supersaturated solution a figure of 10.19 was obtained, indicating a small but significant difference. In the rate-of-growth experiments saturated solutions are obtained by this method.

Oslo Crystallizer

In the E.M.R. contract at Birmingham University on controlled crystallization studies in an Oslo crystallizer (QTR.4/58), a phase of the work has been completed by the first student, Mr. A.G.C. Palmer. This was the determination of the rates of growth of crystals at different heights in the classifying crystal bed, using the system potassium nitrate/water.

The method adopted for the study was to introduce a crystal bed of known size distribution into the apparatus and to run for periods of up to 30 min at a predetermined supersaturation value. The supersaturation of the liquor flowing into the bed was measured by an inductance winding around the inlet tube (see QTR.4/58). After the experiment the crystal bed was withdrawn and its size was determined. From this determination the amount of growth which had taken place was computed on the assumption that the largest particles in the bed at the beginning of the run remained the largest at the end. Growth rates have been estimated in this way for different rates of liquor circulation and have fallen within the range of 1 to 3 microns/minute average linear growth rate for 1 per cent supersaturation. A dependence of growth rate on crystal size, or more properly on the velocity of the flow of solution suspending a crystal, was also noted. Attempts were made todiscover the distribution of supersaturation in the crystal bed by temperature-scanning the bed, by which temperature changes due to heat of crystallization are detected, and it appeared that there was a very rapid relief of supersaturation in the bottom of the bed.

The work is being continued by another student under Dr. Bransom at Birmingham.

XXXI.1.3 Miscellaneous Services

Fine Picrite

100 lb of fine picrite of 80,000 cm^2/cm^3 specific surface has been prepared for propellant work on the substitution of very fine picrite for ammonium perchlorate. The method described in E.R.D.E. Report No. 5/R/51 was followed,

/using .....

using ammonia and formaldehyde as crystal growth modifiers. Difficulty was experienced in obtaining material with similar high specific surface, when using a different, smaller centrifuge. It was found that results on a rotary vacuum filter were as good as those on a small centrifuge and that they could be improved by cooling the cake with a spray of cold water. The method of drying the product was shown to be of great importance; an oven with inadequate ventilation considerably reduced the specific surface. The specific surface was measured by the air-permeability method using the slip correction, as 79,000 cm^2/cm^3.

2-Nitrodiphenylamine

4 cwt of 2-N.D.P.A. have been milled for use in colloidal propellants.

XXXI.2 MANUFACTURING PROCESSES

XXXI.2.1 Picrite Processes

There has been collaboration with R.O.F., Bishopton in connection with the start-up of the picrite plant which utilises the E.R.D.E. direct fusion, and low-ratio nitration, processes.

In the direct fusion process for the manufacture of guanidine nitrate, an impurity, ammonium thiocyanate, accumulates slowly in the plant liquors, probably reaching an equilibrium concentration. This concentration depends upon the sulphur content of the nitrolim but would normally be expected to reach 0.2 - 0.3 per cent by weight of ammonium thiocyanate. In normal operation of the plant, the liquors, which are alkaline with ammonia, are neutralised with 55 per cent nitric acid to pH 6. It was desirable to know the effect of the addition of excess nitric acid arising from faulty operation; when such a liquor is acidified with nitric acid there may be a vigorous gas evolution (oxides of nitrogen, hydrogen cyanide) depending upon the temperature and pH.

Experiments have been carried out which indicate that above pH 2.0 no reaction occurs at temperatures below 100°C when the thiocyanate concentration is 0.3 per cent. In more acid liquors, at less than pH 0.5, the reaction may commence below 50°C. Using the more acid solutions confined in a sealed tube a pressure of 30 p.s.i. is produced within 15 seconds, but when there is a capillary tube vent a pressure of only 3.8 p.s.i. is produced. Confinement does not affect the temperature at which the reaction commences.

From the results it was possible to calculate the maximum rate of discharge through the capillary vent. Scaling this up to the plant scale, in which the neutraliser has a capacity of 140 gallons, the maximum flow rate would be 80,000 lb/h of liquid. By successive approximation this can be shown to require a 2-inch bore pipe if the pressure is to be limited to 5 p.s.i. when the pipe is 30 ft long.

On the large-scale plant a 2-inch pipe to atmosphere has been fitted and in addition there is a 3-inch connection to the decanter. The effect of a vigorous decomposition would therefore be limited to the discharge of vapours in the vicinity of the decanters. Therefore, faulty operation could give rise to hazard from fume, but not from pressure burst.

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The layout of the nitration plant and its inherent safety in the event of a fume-off in the nitrator has been studied. Premixing of oleum and recycle liquor before they entered the nitrator was advocated and has been incorporated.

There are two possible types of decomposition which have different effects and have to be studied separately. When the picrite content of the mixture is high, a hot spot will initiate a highly exothermic reaction which will propagate through the mass rapidly with considerable violence. Experiments confirmed that although the picrite content is high enough in the nitrator the premix eliminates the source of any hot spots. The premix composition could not be initiated in this way, having too low a picrite content.

The other mechanism is slow heating, either self-heating or applied. Experimental results show that the nitration mixture is stable up to 95°C, whereas the premix composition fumes off at around 60°C. Pressures have been calculated for the fume-off of this mixture and show it to be quite safe in the present plant. The mechanism has been studied and found to be concurrent hydrolysis to guanidine nitrate and degradation to urea. The urea then reacts with the nitric acid from the hydrolysis to give nitro-urea which is unstable. This explains the gas analysis of 80 per cent N_2O and 20 per cent CO_2 at temperatures below 120°C. The amount of decomposition was measured under different conditions of temperature, acid strength and concentration and found to correspond to a loss of yield of two or three per cent in a Bishopton premixer. The ideal premixer design would be of as small a volumetric capacity as is consistent with the necessary cooling area. Such a vessel is being designed.

XXXI.2.4 Polyurethanes

Polyesters

The 25-gallon reaction vessel has been replaced by a 50-gallon one. This allows an output of 150 gal/week of modified polydiethylene adipate or 200 gal/week of F.S.7, with 24 h shift working. Two blending tanks have been installed, and polyester batches can now be blended into lots up to 300 gallons.

Since last September, 130 gallons of modified polydiethylene adipates and 1620 gallons F.S.7 have been made; some purchased polyester consignments have been blended to give a standardized lot.

Isocyanates

Twelve new isocyanates (listed below) have been prepared in 1 to 5 lb quantities. All were prepared by phosgenation of the amine by the method given in B.P. 806,903 and purified by vacuum distillation, except that No. 12 had to be purified by recrystallization from petroleum ether. Yields were about 80 - 95 per cent of theory, except for n-butyl isocyanate which was unstable during the phosgenation giving appreciable quantities of butyl chloride. All the amines were available except those for Nos. 2 and 12, which were prepared by reduction of the nitro-compounds by hydrogenation. An assessment of the methods available for the production of isocyanates has been made and a small-scale continuous plant has been designed; it would be used if larger scale manufacture is required.

/No. .....

No. 1	-	Benzyl isocyanate	
2	-	1-Chlorbenzene-2,4-di-isocyanate	2 lb,
3	-	p-phenylene di-isocyanate	5 lb,
4	-	m-chlorophenyl isocyanate	1 lb,
5	-	o-chlorophenyl isocyanate	1 lb,
6	-	p-methoxyphenyl isocyanate	1 lb,
7	-	o-methoxyphenyl isocyanate	1 lb,
8	-	p-tolyl isocyanate	5 lb,
9	-	n-butyl isocyanate	1 lb,
10	-	p-nitrophenyl isocyanate	1 lb,
11	-	o-nitrophenyl isocyanate	1 lb,
12	-	2-methyl-5-cyanato-N-phenyl ethyl carbamate	20 g.

Polyurethane Propellant Mixing

Assistance has been given in the design of the new batch-mixing plant to be installed in the Composite Propellant Section, and particularly in the preparation and feeding of raw materials.

Considerable progress has been made in investigations on a continuous mixing process; work has centered on: (a) the mixer design, (b) control and measurement of the feed flow rates and product flow from the mixer, and (c) continuous de-gassing. The mixer has been made larger, of 3 inches diameter, but retaining the simple design outlined in QTR.3/59. The liquid feeds present no problems, and the heated aluminium and ammonium perchlorate feeds have been made satisfactorily by developing steam-jacketted, vibrator, weighing feeders. So far, this work has been restricted to dummy propellant, loading with aluminium in place of perchlorate. It has become evident that the flow properties of live propellant will be different, may be very variable with composition at the high oxidizer loadings contemplated, but are of critical importance in a continuous mix system where accurate control of feed and propellant flows is absolutely necessary. Therefore little further progress can be made under items (a) and (b) except by working with live propellant. Such a programme would require considerable amounts of propellant and would have to be assessed in conjunction with S.P.R.I. As the production requirements are likely to be small, continuous mixing may be justified only if the process and plant can be engineered in a simple and cheap form.

However, it has been possible to experiment on continuous degassing and casting (item (c)) with live propellant, using 20 lb lots of propellant made by mixing for only 3 minutes in a small batch mixer. The mix was made at atmospheric pressure and was allowed to run continuously at a rate of 2 to 3 lb/minute through a vacuum degasser and into a vacuum casting vessel. The degasser was a steam-jacketted vacuum vessel in which the mix stream flowed through two horizontal plates each having 75 × $\frac{1}{4}$-inch diameter holes.

/The .....

The degassed propellant flowed into a polythene mould in the casting vessel, and could then be cured and taken from the mould for testing.

The final product was free from visible gas bubbles and within 0.005 of the theoretical density. Even after removal of one tray, and finally both trays, the density was still within the specified limits. Using no trays a 1-inch diameter inlet direct into the evacuated chamber seemed to suffice for degassing, provided the rate was controlled to 2 to 3 lb per minute. Attempts to degas freshly mixed propellant by applying vacuum to it in a receiver without passing it through a degassing chamber were not successful, the density being low (1.759) and gas bubbles visible.

It has thus been shown that degassing can be effected, and a satisfactory propellant made, by a simple continuous vacuum degassing of the product from an atmospheric mixing operation. The remaining problems of an integrated continuous process are control of the feed and product flows.

XXXI.2.5 Ammonium Perchlorate

The study of the improved ammonium perchlorate process showed its advantages when the feed of sodium chlorate was free from chloride. The effect of chloride addition arising from the build-up of electrolysis impurities has been studied and it has been shown that the chloride ion has a small effect on the first stage. It reduces the solubility of ammonium perchlorate in the ammonium - sodium - perchlorate - carbonate system which increases the yield of perchlorate in the first stage without decreasing its purity.

The corrosion rates of FDP and FMB stainless steels and 99.5 and 99.9 purity aluminium were studied at 50°and 100°C. A number of synthetic liquors with and without chloride as impurity, and representing both the Minsterley process and the improved process, were used in the tests which lasted 90 days. The conclusions were:

(i) FMB and FDP stainless steels were suitable for use with the improved-process liquors, even in the presence of chloride at 50° and 100°C.

(ii) Aluminium showed appreciable corrosion with the improved-process liquors at 100°C.

(iii) Neither aluminium nor stainless steel would withstand the Ministerley plant liquors at 100°C; FDP stainless steel suffered such severe corrosion that it fell to pieces on handling.

It is evident that there is no prospect of improving the Minsterley plant yield, with its 15 per cent loss to waste of perchlorate radical, without an evaporator, piping and auxiliary equipment constructed of a special metal, possibly one of the Hastelloys. This need does not arise in the improved process, and is a further argument in favour of its adoption at R.O.F., Bishopton.

Grinding and Size Separation

The separation of ammonium perchlorate, after grinding, into particles of different size ranges was undertaken with the object of making available experimental quantities of 100 - 500 lb/day. The preferred specific surfaces were 1500 - 2500 etc, up to 7,500 - 8,500 cm^2/cm^3.

/The .....

The initial attempts to carry out the operation with simple apparatus - cyclone, gravity settling box, air elutriator and air riffling table - showed that the principal difficulty was aggregation. A study of the problem showed that aggregation, together with some crystal growth, occurred at all relative humidities of air down to 5 per cent or less, so that the first step was to set up a silica gel drier to give a supply of adequately dried air. This air was supplied to a grinding mill and the airborne, ground product was tested in the cyclones and gravity settlers. Cyclonic separation has limitations for classifying particles of diameters above 10 microns, and it was considered that a rotary centrifugal separator should be more effective, especially for larger throughputs. A centrifugal machine was designed from first principles and was constructed as simply as possible from aluminium sheet. Since low speeds only were needed oil-free bearings of Teflon were used. The separator is fed with ammonium perchlorate from the mill, of mixed size distribution; it is designed to separate the material into two size fractions; the point of division is controlled by the separator speed and the airflow through it.

Preliminary tests have been carried out and the equipment appears to operate effectively. Reasonably sharp separations have been obtained at the rate of 10 lb/h, and work is continuing.

XXXI.2.6 Lead Compounds

Production of "lead stannate" has continued at 55 lb/week. Three 45 lb batches of lead phthalate have also been made.

XXXI.2.7 Nitric Esters

Both diethylene glycol dinitrate and triethylene glycol dinitrate have been made in quantity, 890 lb of the former and 400 lb of the latter, by the batch process, drowning out the nitration mixture in water.

Attention has been given to the intensive drying of nitric esters for experimental batches of polyurethane propellant. Vacuum drying of T.E.G.N. was shown to reduce the water content from 0.6 to 0.1 per cent in 1 hour at 60°C. This was almost the equilibrium water content for 10 mm Hg, at which pressure the T.E.G.N. vapour pressure was negligible. From the information obtained on vapour pressures, using Henry's Law, the amount of dry nitrogen required to dry a 5 lb batch to 0.01 per cent water content was calculated as 14 litres. In the experiment 16 litres were used. In all 28 lb of T.E.G.N. have been dried in this way and, using the same technique, 16 lb of dry D.E.G.N. have been prepared. With an improved apparatus 10 lb can be dried per batch.

Some study has been made of a tubular reactor for nitric ester preparation, and the work has been given impetus by the difficulty of nitrating butane-1:4-diol. It has been found that there is a small trace of an unidentified impurity in the diol which will produce a fume-off of the reaction mixture. This impurity can be removed by a lengthy efficient fractionation but some element of risk remains. Moreover, it has been found that the I.C.I. Relative Stability of Separation test indicates that the nitration mixture is quite hazardous compared with glycerine nitration mixture. Little warning of an impending fume-off would be expected and the temperature at which a runaway temperature rise starts is about 70° instead of 100°C. In view of these observations a tubular reactor was devised, similar in many ways to the Gyttorp injector nitrator but having metered feeds in place of an injector system.

/The .....

The nitrator consists of a small mixing chamber with a tangential acid inlet and a central glycol inlet discharging through a restriction into a reaction tube, fitted with turbulence promoters. With a high acid/glycol ratio of 20:1 by weight, a reaction temperature of $25^{\circ} - 30^{\circ}$C is expected. The short residence time of five seconds is likely to give over 95 per cent conversion to the nitrate and the relatively small quantity of detonable material in the tube will make the operation easy to protect. The nitration mixture is "drowned out" by discharging into excess of water.

The nitration is being conducted by remote control up to the stage where all the glycol has been fed and the apparatus has been flushed through with mixed acid. Separation of the product from the diluted acid will then proceed in the normal way.

/XXXII .....

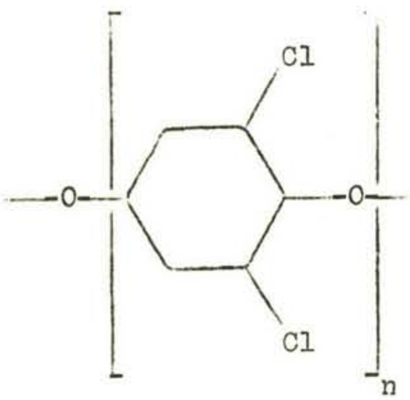
XXXII ANALYTICAL CHEMISTRY

XXXII.1 ANALYSIS

Differential Thermal Analysis

The thermal polymerisation of a monomeric anthracence derivative was studied. Polymerisation was indicated by a very sharp exotherm at 280°C and this was followed by oxidative degradation at higher temperatures. Working in an atmosphere of nitrogen to suppress the oxidation gave a very good thermal record and enabled the heat of polymerisation to be calculated - found: $\Delta H\rho = 46 \pm 5$ kcal/mole.

The technique was also applied in an attempt to detect the occurrence of second-order transitions in polymers of the types:



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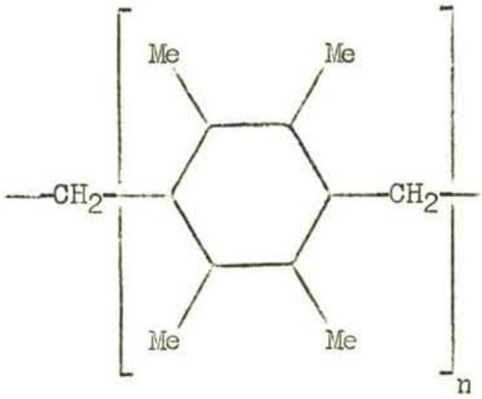

II

The thermograms were complex and no real evidence was obtained for the appearance of such transitions: it is also unlikely on theoretical grounds that D.T.A. would be a suitable method for this since such changes are marked only by a discontinuity in the specific heat curve.

Initiators

Samples of hydrated barium styphnates have been characterised using thermogravimetry. The results showed that Type II contains 1.5 mol. H_2O whereas Types I and III are both monohydrates. However, the latter may be distinguished in that it loses water between 150° and 210°C, whereas Type I is thermally stable up to 200° - 210°C becoming anhydrous only at 245°C. A sample consisting of a mixture of Types I and III dehydrated over the range 150° - 245°C. Type II when treated with water was shown to become a monohydrate and its dehydration temperature range of 210° - 245°C showed it to have changed to Type I.

The ultra-violet examination of tetrazene has been successfully applied to R.D.1357, although the presence of the surface active agent, Belloid TD, may cause slight interference under certain conditions.

Propellants

An improved method has been developed for the determination of acetyl values of polyesters, and a chemical investigation is in progress to

/determine .....

determine the fate of lead salicylate in PU propellants after climatic trials.

Pyrotechnics

Two commercial samples of boron have been examined chemically to establish the reason for their different behaviour in flare compositions containing potassium perchlorate. The results were as follows:

Sample	"Trona"	"Mule-team"
Boron content, per cent	90.6	87.4
Water insolubles, per cent	2.8	16.1

The "Mule-team" sample appears to contain an inert impurity which causes it to be less reactive. Thermogravimetry and D.T.A. experiments showed no differences between the two samples.

XXXII.2 COMPATIBILITY

Cartridge brass passivated by the sulphuric acid/dichromate processes devised by R.O.F., Blackburn and A.R.D.E., and thoroughly washed and dried, did not affect the chemical stability of representative single- and double-base solid propellants and high explosives.

The Northern Rubber Co. Ltd.'s mix CL.2754A, based on Hypalon, a chlorosulphonated ethylene rubber, was chemically compatible with cordite condensates, and only slightly incompatible with double-base solid propellants. A lead-free version (employing magnesia instead of litharge), CL.7888, was chemically compatible with a typical ammonium picrate/ammonium perchlorate plastic propellant. Bostik White Sealing Strip, a vegetable oil/chalk/asbestos mixture, intended for use in the same motor case (Blue Water), behaved similarly to CL.2754A.

A series of vulcanised natural rubber mixes, with various accelerators and degrees of cure, has been examined for compatibility with double-base propellants. Most of them were fairly satisfactory, given adequate curing times, as regards chemical compatibility with propellant SC, the accelerators MBT, MBTS, thiocarbanilide and carbamite being somewhat better than Guantal and Ureka Base. However, all vulcanised natural rubbers deteriorate physically in proximity to double-base propellants.

In connection with an enquiry into a fire which occurred in a Naval catapult at R.A.E., Bedford, Oil M.160 and propellant SC employed in the equipment were examined for compatibility. The chemical stability of the propellant was unaffected by the oil, and interaction was therefore unlikely as a cause of the incident.

Three weedkillers, A489, A894 and A896 (Fisons Ltd.), based on triazines (see Geigy CP/3/58, QTR.3/58) were incompatible with a representative double-base solid propellant, and with representative high explosives, but did not reduce the chemical stability of gunpowder.

/Aroclor .....

Aroclor 1248 and Aroclor 1254 (Monsanto Chemicals Ltd.) possible plasticisers for double-base solid propellants, did not reduce objectionably the chemical stability of a representative double-base non-picrite propellant.

Sorboprene 70 (Sorbo Ltd.), a foamed ester-type polyurethane, was tested, together with material containing a 10 per cent excess of tolylene di-isocyanate, for effect on single- and double-base propellants and high explosives; additional trials covered both materials after humid-atmosphere storage up to 3 months at room temperature. Both normal and "10 per cent excess" material were satisfactory for contact under dry conditions with the propellants, but not with high explosives other than tetryl.

Monobasic cupric salicylate ($CuO.Cu(C_7H_5O_3)_2$, National Lead Co., U.S.A.) added experimentally (2 per cent) to a cast double-base propellant did not affect its chemical stability to an objectionable extent.

Polypropylene ("Propathene") type GWM-02 (I.C.I. Ltd.) was chemically compatible with representative single- and double-base propellants, cordite condensates, nitroglycerine, representative high explosives and gunpowder.

Cotton cambric dyed with Chlorazol Union Yellow (I.C.I. Ltd.), for cartridge bags, was chemically compatible with propellants N and NQ.

The polyester resins, Cellobond AX 2710 (British Resin Products Ltd.), Hetron 92, Hetron 32A and Vibrin 121 (all three of U.S. origin), cured for 4 hours at 60°C with catalyst and accelerator, all reduced the chemical life of a colloidal rocket propellant to an appreciable, but not (in view of other life-determining factors) unacceptable, extent.

Tensol Cement No. 50 (I.C.I. Ltd.), after air-drying for 3 days at room temperature and curing for 10 minutes at 100°C followed by 20 minutes at 150°C, did not reduce the chemical stability of 60/40 RDX/TNT.

Work in collaboration with the Materials Research Group to develop a completely compatible butyl rubber vulcanisate has led to a formulation which has been checked as chemically compatible with representative single- and double-base solid propellants, plastic propellants (picrite/perchlorate type) and cordite condensates, and with representative high explosives and gunpowder.

Sellotape was considered not to create a hazard in use on solid propellant surfaces for strictly limited periods (a few months), although it reduced the life of several propellants appreciably. It was found sufficiently compatible for use in contact with a Ballistite A/gunpowder mixture in an igniter.

Lustrex T.11 high impact polystyrene (Monsanto Chemicals Ltd.) was found chemically compatible with double-base propellants.

Iron and steel processed by the "Sulfinuz" surface treatment (I.C.I. Ltd., General Chemicals Division) did not affect the chemical stability of high explosives or of pyrotechnic compositions thought likely to react with the sulphur-containing constituents of the surface layer formed.

Two mouldings in the glass-filled alkyd resin A.M.C. 440A (Black) (Resinous Chemicals Ltd.) were chemically compatible with tetryl, RDX and TNT.

Fully-cured Cement R.D.1286 was no less incompatible with amatol than freshly-prepared material.

/Phoengard .....

Phoengard electrically-conducting flooring (Phoenix Rubber Co. Ltd.) has been found satisfactory from both electrical and chemical aspects for floor or table coverings for operations with propellants, high explosives, gunpowder and initiators.

A flexibilised epoxy resin (Epikote 828, Thiokol LP3, Hardener K.61B), air-cured for six weeks, was chemically compatible with tetryl, but slightly incompatible with RDX and TNT.

Three plastic/glass laminates, SP, X.250 and G.9 (Mica and Micanite Ltd.) were chemically compatible with tetryl, RDX and TNT, although G.9 was more alkaline than desirable with TNT.

Saroy Styron 475 high impact polystyrene (Saro Laminated Wood Products Ltd.) proved satisfactory for contact with gunpowder and S.R. 371C, but with propellant PU undesirable chemical and physical interactions occurred.

Polyethylene compound DND 0400 (Bakelite Ltd.) and a similar polymer XPX 22938 containing 100 times the content of antioxidant, did not affect the chemical stability of representative high explosives and single- and double-base propellants or gunpowder.

The three components of the Ardrox No. 996 flaw detection process (Brent Chemical Products Ltd.), viz: penetrant, penetrant remover and developer, after light spraying on to a double-base propellant and air-drying, did not affect its chemical stability.

A modified butyl rubber for the improved Baby Viper hose, with lower sulphur and higher accelerator contents than previous material (see QTR.2/59), was chemically compatible with tetryl and 60/40 RDX/TNT.

Bostik Adhesive No. 1261 (B.B. Chemicals Ltd.) in the form of an air-dried film was chemically compatible with plastic propellant R.D.2408.

Florube Grease W (I.C.I. Ltd.), a chlorofluorohydrocarbon, was found suitable from the compatibility aspect for use as lubricant in colloidal propellant incorporators.

An epoxy potting composition based on Araldite Resin F, hardener 905 and accelerator 905C, cured 24 hours at 120°C, was satisfactory for contact with double-base solid propellants; another, containing more 905C and cured for 8 hours at 80°C, was doubtful in this respect. Both were chemically compatible with high explosives except amatol.

The pigmented phenolic-resin-bonded P.T.F.E. coating, Emralon 810 (Du Pont de Nemours via Acheson Colloids Ltd.), when applied to steel and cured one hour at 150°C, did not affect the chemical stability of propellants SC and PU, and affected the heat test value of nitroglycerine only negligibly.

Undried and dried samples of Varnish R.D.1198, both without and with one per cent of the dyestuffs, Solvent Blue 3, Solvent Green 1, Solvent Black 7 and Stearated Solvent Black 7, were found satisfactory for use with lead azide.

A rubber purporting to be to C.S.2876, but containing a West African rubber in place of the Hevea Brasiliensis normally used, was chemically satisfactory for contact with a representative picrite-based propellant and with cordite condensates.

/Igniter .....

Igniter composition P.N.772, prepared by mixing S.R.252 with a solution of pyroxylin in acetone, was found not to affect the chemical stability of smoke composition P.N.765, when poured over the latter and allowed to dry.

A sample of phenol-formaldehyde lacquer to C.S.2465A (S.E. Porter and Sons Ltd.) was examined to the compatibility clause and was found after stoving (30 min. at 115°C) to be chemically compatible with double-base solid propellants and 60/40 TNT/Al, tetryl, pentolite, and torpex 4A but not with amatol. Two samples (Thornley and Knight Ltd.) to the same requirements were found after stoving (30 min. at 300°F (149°C)) to be chemically compatible with gunpowder and propellant FNH. Both affected propellant NQ to an extent considered negligible in the circumstances of use and both were chemically compatible with representative high explosives.

An air-dried film of the adhesive Atlas Plastik Kleber 5C0 (Agents: Bush Beach and Segner Bayley Ltd.) was chemically compatible with RDX, TNT and tetryl, as also was one produced by admixture with the material of 10 per cent, of its weight of "Zusatz II", an addition agent designed to give improved bond strength and heat resistance.

The stability of ammonium perchlorate was unaffected by addition of up to 5 per cent of molybdenum disulphide for improvement of flow properties.

XXXII.3 STABILITY

Initiators

Trials on the new R.D.1357 tetrazene at 140°F (60°C) and 95 per cent r.h. show that it is likely to be just as stable as commercial tetrazene under these conditions.

Propellants

Further modifications have been made in the design of new storage tanks for the modified silvered vessel test on high impulse propellants. These modifications include additional safeguards against the effects of ignition.

Ignitions accompanied by small fires have occurred during silvered vessel tests on casting powders containing ammonium perchlorate and further testing has been confined to the finished cast propellants. The results indicated that under the silvered vessel test conditions, high impulse compositions were somewhat less stable than Propellant Mk. I; the inclusion of nitroguanidine produced a marked improvement in stability. Resorcinol in addition to the normal stabiliser was also beneficial. A report on this work has been published (E.R.D.E. Report No. 7/R/60).

A considerable number of conventional silvered vessel tests have been carried out on experimental batches of E.R.D.E.-manufactured extruded and cast platonised compositions. The chemical stability of these compositions is, in general, good.

Propellant samples have been examined for chemical stability in connection with the following storage trials:

/(a) .....

(a) PU charges from O.B. trials on 2-inch air to air Mk. I rocket motors,

(b) Foreign propellant from 100 mm Blindicide H.E.A.T. rocket motors,

(c) Cordite SUK manufactured from Indian N.C.,

(d) Powfoot S.A. propellant,

(e) Miscellaneous samples from cracking trials on E.R.D.E. experimental manufactures.

Advice has been given on sentencing of Service propellant types so far not included in the current "Guide to the Sentencing of Bulk Propellant", and information on other experimental types for which the normal test procedure is of doubtful value is being reviewed for sentencing proposals.

The apparatus designed for the continuous measurement of NO_2 from heated propellants has been used to study the early stages of the decomposition of high-impulse compositions. Gas evolution measurements using mixtures of N.C. and ammonium perchlorate in a vacuum apparatus at 157°C show that the ammonium perchlorate increases the rate of decomposition of N.C. by a factor of about 1.5. This is not high, but the nature of the results suggests that at high temperatures the catalytic effect of perchloric acid is much reduced by its volatility.

In order to work in more realistic temperature ranges (50° - 60°C) the NO_2-measuring apparatus is being rebuilt to improve its sensitivity. An isothermal micro-calorimeter is also under construction to study spontaneous self-heating in this temperature range.

Polyurethane Propellants

All samples submitted show that no fuming or self-heating is obtained after 2000 hours at 80°C in standard silvered vessels. Taliani tests in nitrogen failed to produce a significant gas pressure in 5 hours at 119°C in the case of composition U223. Compositions U216, U224 and U147/3 also gave no gas in 5 hours at 100°C.

Safety Certificates

Stability investigations have been carried out, in connection with the preparation of safety certificates, on:

High Explosives

Cyclotol, Composition B3, and the U.K. and U.S. forms of PBX/E.

Propellants

Plastic propellant R.D.2410.

Pyrotechnics

Priming composition IT7.

Chemical stability was satisfactory in all instances.

/XXXII.4 .....

XXXII.4 SERVICES TO BRANCHES

Analysis

During the period under review, 1450 samples have been received and examined. These included Service experimental propellants, polyester resin 422, German propellant Gudol RP95, various calcium phosphates, copper soaps and a variety of lead salts. Of the propellant samples completely analysed, 50 were new compositions for which no written methods were available.

Satisfactory analytical methods have been developed for:

(a) Perchlorate, aluminium and nitroguanidine in high impulse propellant. A Technical Memorandum is in draft,

(b) Resorcinol in newly manufactured and aged high-impulse propellants,

(c) Control of solid products and mother liquors in the new ammonium perchlorate process being developed in E.R.D.E.

Hot and Cold Climatic Facilities

The use by other Establishments of the facilities provided by the hot and cold chambers on the South Site has continued. Following a fully-instrumentally-recorded cycling trial of equipment for R.A.E. in the hot and cold chambers, another trial involving low temperature storage tests on R.A.E. equipment using electric blankets was carried out. In conjunction with I.F.V.M.E. and Frigidaire Ltd. cold storage test trials were carried out on blood storage cabinets and an O.B. cycling trial on A/T mines on behalf of A.R.D.E., Woolwich.

Boron Hydride Derivatives

(i) Decaborane Grignard Reagent

$B_{10}H_{13}MgI$ produced by the reaction of decaborane with methyl magnesium iodide has hitherto been regarded as a Grignard reagent. Its ^{11}B nuclear magnetic resonance in ethereal solution has now been measured and shown to be very similar to that of the sodium salt of decaborane $Na^+B_{10}H_{13}^-$. This implies that the substance should be regarded as a salt $[B_{10}H_{13}]^-MgI^+$. Moreover, it has also been found that a similar product is formed by the action of Me_2SO_4 on $NaB_{10}H_{13}$.

(ii) Decaborane reacts with a number of electron donors, M, according to the equation

$$B_{10}H_{14} + 2M \rightarrow B_{10}H_{12}M_2 + H_2$$

Hawthorne and Pitochelli (J. Amer. Chem. Soc., 1959, 81, 5519; 5833) have shown that where M = Et_3N, two isomers exist - a covalent $B_{10}H_{12}(Et_3N)_2$ and an ionic $[B_{10}H_{10}]^{2-}$ $[Et_3NH]^+_2$. The infrared and ^{11}B nuclear magnetic resonance spectra of a number of these compounds have been meaured to decide whether they have the ionic or covalent formulation. Only triethylamine was found to give an ionic isomer. The remainder were all covalent - where M is Me_2S, MeCN, $Et_2N.CN$, C_5H_5N, 2-C_5H_4BrN, $HCONMe_2$, $MeCONMe_2$.

/A .....

A number of reactions where one ligand is displaced by a second have been studied and it is possible to write a series

$$\left.\begin{array}{l} C_5H_5N, \\ \\ Et_3N, \\ \\ (C_6H_5)_3P \end{array}\right\} > \left.\begin{array}{l} CH_3CONMe_2, \\ HCONMe_2 \end{array}\right\} > CH_3CN > Me_2S$$

where substances will displace all those to their right. The infra-red spectra of the $HCONMe_2$ and CH_3CONMe_2 compounds indicate that they are coordinated to the $B_{10}H_{12}$ residue through the carbonyl oxygen.

(iii) The reaction between pyridine and decaborane has been examined in detail. Previously, Burkardt and Fetter had reported that the reaction was complex, but they had isolated a derivative $B_{10}H_{14}(C_5H_5N)_3$ (red). It has now been found that this substance readily loses one molecule of pyridine and one of hydrogen in vacuo at 100°C, to give $B_{10}H_{12}(C_5H_5N)_2$. Similarly, treatment with dry ether yields pyridine, $B_{10}H_{12}(C_5H_5N)_2$ and hydrogen. The substance must be regarded as $B_{10}H_{14}(C_5H_5N)_2$ with one molecule of pyridine of crystallisation. An isomeric form $B_{10}H_{14}(C_5H_5N)_3$ (red) is formed by precipitation on mixing n-hexane solutions of decaborane and pyridine. This substance only loses pyridine at 160°C in vacuo to give $B_{10}H_{12}(C_5H_5N)_2$. Furthermore it is formed as a by-product when $B_{10}H_{14}(C_5H_5N)_3$ is treated with ether.

Dilute solutions of decaborane in benzene can be shown from the ultra-violet spectrum to react with dilute pyridine according to the equilibrium

$$C_5H_5N + B_{10}H_{14} \rightleftharpoons B_{10}H_{14}\cdot C_5H_5N$$

Stronger solutions precipitate a yellow-red mass which on heating gives H_2 and $B_{10}H_{12}(C_5H_5N)_2$. It is most probable therefore that the behaviour in benzene solution can be represented thus

$$\begin{array}{l} C_5H_5N + B_{10}H_{14} \rightleftharpoons B_{10}H_{14}C_5H_5N \xrightleftharpoons{+\,C_5H_5N} B_{10}H_{14}\cdot(C_5H_5N)_3 \\ \hspace{16em} \big\downarrow \text{ unstable in solution} \\ \hspace{15em} B_{10}H_{12}\cdot(C_5H_5N)_2 \end{array}$$

/(iv) .....

(iv) The steric conditions of the reaction

$$B_{10}H_{14} + C_5H_5N \rightleftharpoons B_{10}H_{14}\cdot C_5H_5N.$$

have been studied by the measurement of equilibrium constants. Reaction only occurs easily when one α -position in the pyridine is unsubstituted. Thus α-methyl pyridine reacts easily, α,α'-dimethyl pyridine only with difficulty. Quinoline reacts; acridine, 2-methyl, and 8-methyl quinolines do not. Similarly, when decaborane is substituted at the 6-position, and to a lesser extent the 5-position, reaction is considerably hindered.

Infra-red Spectroscopy

(i) Routine identifications and analyses have been carried out on thirty-eight batches of samples of widely differing constitution.

(ii) The spectra of a number of organo-sulphur compounds including $(MeO)_2SO$, $MeSO_2Cl$, $(MeO)_2SO_2$, and $MeSO_2OMe$ have been measured as reference substances for identification of reaction products from dimethyl sulphate methylations. Rotational isomerism has been shown to occur in several of these compounds.

(iii) The measurement of the spectra of some aliphatic and aromatic nitrosamines and four aromatic nitramines has been completed. Key bands have been assigned to vibrations of the N-NO group.

(iv) Spectra of a number of acetyl derivatives of organo-nitrogen compounds have been measured in order to determine their structure.

Gas Chromatography

Propellant Analysis

The method for the estimation of ethyl and methyl centralites, and diphenylamine outlined in QTR.3/59 is now being used for the routine estimation of residual stabilisers in propellants from climatic and other trials.

A satisfactory method has been developed for the estimation of 2-ethylhexoic acid (from lead 2-ethylhexoate). The propellant sample is dissolved in aqueous alkali, and the solution is acidified and extracted with ether to remove the 2-ethylhexoic acid. The acid is estimated by chromatographing part of the extract, to which is added a suitable internal standard, e.g. 1,2,4,5-tetramethylbenzene. The stationary phase is a mixture of 9 parts dinonyl sebacate and 1 part sebacic acid, mixed with "Embacel" kieselguhr in the usual way, and the column temperature is 155°.

Rubber samples which had been in contact with charges of PU propellant during hot storage and temperature cycling trials have been analysed for the migrating propellant ingredients. Acetone extracts of the rubbers were chromatographed at 220°C on a polypropylene sebacate column to determine dibutyl phthalate and carbamite, and at 140°C on an Apiezon L column to determine nitroglycerine and 2-ethylhexoic acid. The most heavily contaminated sample, which had been stored for 6 months at 120°F (49°C), contained 8.9 per cent N.G., 4.0 per cent D.B.P., 0.7 per cent carbamite and 0.9 per cent 2-ethylhexoic acid.

/Gas .....

Gas chromatograms of an ether extract of a PU propellant showed the extent of plasticiser migration into the propellant from its ethyl cellulose inhibitor. The sample, taken from near the cuter edge of a Gosling charge, contained 0.8 per cent diethyl phthalate (from the inhibitor), 0.5 per cent dimethyl phthalate (from the cement used to attach the inhibitor), and 4.6 per cent dibutyl phthalate.

A sample of air, taken from the chamber containing the PU propellant starter of an isopropyl nitrate power unit for Sea Slug, contained isopropyl nitrate and methanol vapour. Applying the technique previously used for the estimation of residual solvents, the amount of I.P.N. absorbed by the propellant was found to vary between 3.6 per cent at the surface and 2.8 per cent near the centre of the charge. No methanol was absorbed.

Miscellaneous Analyses

Over eighty miscellaneous samples have been examined, including reaction products from alkylations of decaborane, samples of cyclohexanone containing cyclohexanol and water, and products obtained by reacting free methyl radicals (from tertiary butyl peroxide) with ethyl nitrate, ethyl nitrite, isopropyl nitrite or nitroethane. The most satisfactory stationary phase for the last group of samples, some of which contained as many as fifteen components, was a mixture of 3 parts tritolyl phosphate with 2 parts polyethylene glycol (400), except for the products from isopropyl nitrite where dinonyl phthalate was used.

Analysis of Polyesters

Retention volume values have been obtained for the acetates of 24 polyalcohols used in the manufacture of polyesters. In some cases the polyalcohols can be chromatographed, but in general the acetates are more suitable for gas chromatography. The stationary phases used were polypropylene sebacate, and, for the less volatile acetates, Apiezon L grease. The usual linear relationship between log V_R and number of carbon atoms was obeyed by the acetates of the series, $CH_2OH\text{-}(CH_2)_n\text{-}CH_2OH$ (n = 0 to 4), and $CH_2OH\text{-}CHOH\text{-}(CH_2)_n\text{-}CH_2OH$ (n = 0 to 3).

Preparative Chromatography

The diethyldecaboranes from Hical 3 have been split into fractions and examined by infra-red and nuclear resonance spectroscopy. The fractions consisted principally of the three possible isomers obtained by disubstitution in the 5, 7, 8 and 10 positions, but, since these positions are equivalent, identification of the individual isomers was difficult. The spectra confirmed that no apically substituted isomer was present.

Pure specimens of alkyl decaboranes have been isolated from a number of reaction products, and several fluorinated ketones have been purified using a tritolyl phosphate column.

A study has been made of the effects on column efficiency of changes in operating conditions and column dimensions. The efficiency, in terms of number of theoretical plates, increased almost linearly with column length, but comparison of columns of 1 inch and 2 inches diameter showed that in separating large samples the performance of the 2-inch column was not a great improvement over that of the 1-inch column.

/Maximum .....

Maximum efficiencies for the 1-inch column were obtained at flow rates of 85 litres/hours hydrogen carrier gas and of 22 l/h nitrogen carrier gas, and were about 50 per cent higher in the case of nitrogen. Hydrogen as carrier gas thus gives greatly reduced retention times. The somewhat lower column efficiency may be increased if necessary by using a longer column, and in this case retention times are still much shorter than when using nitrogen carrier gas to obtain the same separating power.

XXXII.5 CRYSTALLOGRAPHY OF EXPLOSIVES, PROPELLANTS AND INITIATORS

Tetrazene

Tetrazene hydrobromide has been prepared in the form of well-crystallised needles and a preliminary investigation has been made to assess the suitability of this substance for use in the X-ray determination of the crystal structure of tetrazene. It has been chosen in an attempt to make a direct determination of the structure, with no assumption regarding packing, bond lengths, etc.

The hydrobromide belongs to space group $P\ 2_1/a$ and its unit cell contains four molecules in general positions. From its optical and cleavage properties, it is most likely that the crystal contains planar molecules arranged with their planes perpendicular to the needle axis, which is the crystal b-axis.

The h0l X-ray intensities have been measured using copper radiation and have been used in the computation of a two-dimensional Patterson synthesis; from these results it has been possible to locate the bromine atoms in the b-projection.

It has been assumed that the contribution of the bromine atoms to the intensities of the diffracted beams is sufficiently great to determine the phases of the majority of these beams; the phases of the bromine contributions have therefore been calculated, and these calculated phases have been combined with observed intensities in computations of the two-dimensional projection of electron density in the unit cell on to the b-face. This has been done by the use of Fourier syntheses and difference syntheses. The majority of the atoms are now resolved in this projection, but overlap of the molecules at present prevents an unequivocal interpretation of the molecular shape; this situation was foreseen owing to the unit cell dimensions and it is not expected that difficulty will be experienced in resolving it in the later stages of the analysis.

Oxamide

An examination is in progress of a number of oxamide samples whose ballistic behaviour had been found to be irregular. Impurities were isolated by a procedure chosen to avoid chemical change of the oxamide; it was found that ammonium oxamate and/or ammonium oxalate could be identified in amounts up to about 5 per cent, and that these substances were only partially removed by a simple extraction procedure. A laboratory preparation at $0^{\circ}C$ was found to contain ethyl oxamate.

Some minor impurity constituents remain unidentified. It was thought that one of these might be tetraketopiperazine or its ammonium salt, but as a result of work on these substances this is now considered to be unlikely.

/The .....

The X-ray powder patterns of the oxamide samples as received show no evidence of these impurities, the patterns of which would be very weak for the concentrations encountered. However, most (but not all) of the abnormal samples show marked modifications of the normal oxamide pattern, such as might be expected in the presence of solid solutions or some degree of lattice disorder. It was expected that oxalic or oxamic acids might form solid solutions with oxamide, and it was found that X-ray patterns of oxamide which had been crystallised in the presence of either of these acids showed many features of the modified oxamide patterns.

Summarizing the results so far obtained, it is found that ballistically abnormal oxamides all contain impurities, but do not all give the modified X-ray pattern; however, as most of the samples so far examined gave abnormal ballistics, it will now be necessary to extend the work to normal samples before the relative importance of the two attributes can be assessed.

Aluminized Propellants

It was reported in QTR.2/59 that an unidentified phase had been observed in a deposit formed on a rocket nozzle which had been used with aluminized ammonium perchlorate propellant; it has now been found that the results agree with figures published for aluminium oxycarbide Al_2OC.

Ammonium Perchlorate

X-ray examinations have been made of samples of solids separating during the preparation of ammonium perchlorate from commercial sodium perchlorate. Sodium bicarbonate, ammonium perchlorate and "trona" (sodium sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$) were identified, but in some cases there were small amounts of unknown phases present. In one case, the pattern given by "sodium bicarbonate" was significantly different from that given by the pure substance and the differences suggest the possibility that a sodium bicarbonate solid solution may be present.

9,10-Bis(chloromethyl)anthracene

The examination has continued of the hydrocarbon, believed to be bis-9,10-dimethyleneanthracene, derived from this chloro-compound; the object was to characterise the three forms of the hydrocarbon and to determine their molecular weights. Well-crystallised samples of the B-form have been prepared by percolation of the C-form with chloroform in bright sunlight; these could be preserved in a refrigerator for long periods.

Single crystal X-ray data have now been determined for all three forms; the measurements were made from Weissenberg films and are as follows:

/Table 7 .....

TABLE 7

Parameter	Form		
	A	B	C
a A.	20.54	9.98	10.36
b A.	13.26	13.06	12.85
c A.	8.28	8.54	8.50
β °	109.8	111.9	112.9
Density	1.314	1.338	1.325
Space-group	$P\ 2_1/a$	$P\ 2_1/c$	$P\ 2_1/c$
Molecular weight	840 (Z = 2)	416 (Z = 2)	414 (Z = 2)
	420 (Z = 4)	208 (Z = 4)	207 (Z = 4)
	(Z = no. of molecules per unit cell)		

These space-groups accommodate four asymetric units or two centro-symmetrical units in the unit cell.

The results are consistent with the view that the hydrocarbon has a molecular weight of 417 in all three forms (theory requires 408); in this case no molecular symmetry is necessarily entailed for the A-form, but in the B- and C-forms the molecule must possess a centre of symmetry.

On the evidence presented here, the possibility cannot be entirely excluded that the molecular weight might be 208 in all three forms. In this case the asymetric unit in the A-form crystals would consist of two molecules, but such behaviour is not common. A third possibility is that the molecular weights might be different in the three forms.

/XXXIII .....

XXXIII PYROTECHNIC COMPOSITIONS

Flare Compositions

Results of climatic trials on elastic pyrotechnics are now available. Two series have been tested, one based upon Thiokol LP33, the other on Thiokol LP2, the former having had 1 year under ISAT(B) conditions, the second series 6 months only, yet Compositions made with the softer rubber, LP33, had swollen and softened after 6 months, but the LP2 compositions were unaffected. LP33 compositions appear to show an increase in luminous intensity and also in burning rate as a result of exposure to ISAT(B); LP2 compositions become less bright but there is very little change in burning rate. The hard rubber is much more resistant to storage at 80°C.

A series of comparative colour trials of green flares has been completed, using rubbery and pressed powder compositions. Day and night trials of flares burned on the ground showed that pressed powders were marginally better for colour, but when compositions were projected as stars using the 1-inch Signal Cartridge, the Thiokol-bound system was markedly superior. A further night trial demonstrated that flares bound with Thiokol LP33 gave slightly better colour than did those with LP2. This trial also showed that the presence of a small percentage of elemental boron gave a greatly improved green colour. The influence of environment on the results was very noticeable and this emphasized the need for a less subjective method of comparison.

The 165 mm AVRE Incendiary Shell

Six of these have been filled, each containing ca 32 lb of composition, using a rubbery flare mixture TF 322. No exotherm was observed during 24 hours curing at 70°C. All were fired successfully at Shoeburyness, and upon bursting on the sand threw out large burning pieces. At the request of A.R.D.E., further shells are to be filled for a demonstration.

Composition TF 320 (LP2 14%, Mg grade V_2 57.3%, $NaNO_3$ 28.7%) which burns at 6 s/inch with intensity 140,000 candles/inch^2, has been filled into 1-inch diameter steel tubes and tested by A.R.D.E. Langhurst as a tracking flare. The required performance was obtained.

Priming Compositions

Cured extruded cords of Thiokol rubber/boron/potassium perchlorate priming compositions have been put into $\frac{3}{8}$-inch diameter lead tubes which have then been rolled out to $\frac{1}{8}$-inch diameter. This has produced a steady burning delay which is completely waterproof. Composition IT7 (QTR.3/59) burns at 5 s/inch.

Samples of rubberised primed cambric substitute have been tested in the cartridge, illuminating, $1\frac{1}{4}$ inch. Successful ignition of all three stars was obtained in each of ten cartridges fired.

/List .....

List of Reports Bearing the Grading "Discreet"

Issued by E.R.D.E. in the Period 1.10.59 to 30.6.60

Classifications: S/D = SECRET/DISCREET

C/D = CONFIDENTIAL/DISCREET

R/D = RESTRICTED/DISCREET

Number	File	Classi-fication	Author	Title
7/R/59	WAC/91/06	C/D	W.E. Batty & B. Gilbert	The Chemistry of RDX and HMX
24/R/59	WAC/91/27	C/D	R.M.H. Wyatt	The Electrostatic Spark Sensitiveness of Initiators: Part 5: Further Study of Ignition with Metallic and Anti-static Rubber Electrodes
26/R/59	WAC/91/23	R/D	I. Dunstan & J.V. Griffiths	Analysis of Organoboron Compounds
28/R/59	WAC/91/28	C/D	Idem	The Friedel Crafts Reaction of Ethylene with Pentaborane-9
32/R/59	WAC/91/32	C/D	L.S. Herbert, R.H. Jones & A.W.H. Pryde	The Concentration and Re-use of Spent Acid from the Nitration of Guanidine Nitrate
15/M/59	WAC/92/13	C/D	J.M. Ferguson	The Application of the Time/Temperature Superposition Principle to the Tensile Testing of Polyisobutene and Plastic Propellant
QTR.3/59	WAC/91/33	S/D	-	Technical Report for the Period 1.7.59 to 30.9.59.
1/M/60	WAC/117/01	C/D	J.A. Hicks	Thrust Efficiency in Aluminized Propellants

List of Reports and Technical Memoranda

Issued in the Period 1.10.59 to 30.6.60

Classifications: C = CONFIDENTIAL

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Number	File	Classification	Author	Title
9/R/59	WAC/91/24	R	D.B. Scaife	The Electrostatic Spark Sensitiveness of Initiators: Part 4: Initiation of Explosion by Spark Radiation
12/R/59	WAC/91/09	C	R.L. Williams	The Structures of some Ethylated Derivatives of Pentaborane and Decaborane
21/R/59	WAC/91/18	U	T.J. Lewis & T.M. Walters	The Behaviour of Stannic Acid Sols in Concentrated Hydrogen Peroxide: Part 1: Factors Affecting the Stability of Stannic Acid Sols in Concentrated Hydrogen Peroxide
22/R/59	WAC/91/25	U	Idem	ditto Part 2: The Mechanism of Stabilisation of Hydrogen Peroxide by Sodium Stannate
23/R/59	WAC/91/19	U	J.A. Hicks & D.P. Needham	The Low Pressure Decomposition Flame of Ethyl Nitrate: Part 1: Chemical Kinetics
27/R/59	WAC/91/26	R	A.J. Owen	Thermodynamic Aspects of the Reactions of Boron Hydrides and Related Compounds
31/R/59	WAC/91/31	R	R.P. Ayerst & L.S. Herbert	The Pilot Plant for Guanidine Nitrate by the Direct Fusion Process: Part 2: The Precipitation of Calcium Carbonate and the Separation of Sludge
33/R/59	WAC/91/34	R	H.C. Sayce	The Analysis of Mercury Fulminate and its Application to Fulminate in Storage
34/R/59	WAC/91/35	U	A.J. Dedman & A.J. Owen	Calcium Cyanamide Synthesis: Part 4: The Reaction $CaO + CO_2 \rightleftharpoons CaCO_3$

Number	File	Classification	Author	Title
5/M/59	WAC/92/05	C	J.K. Clark	The Gun Assisted Rocket: Sensitiveness of the Propellant Filling
11/M/59	WAC/92/09	R	J. Powling & W.A.W. Smith	Rates of Burning and Flame Temperatures of some Diluted Nitric Ester Mono-propellant Systems
12/M/59	WAC/92/10	C	C.H. Peers	Plastic Propellants Based on Ammonium Nitrate: Their Rheology and Ballistics
14/M/59	WAC/92/11	C	A.R. Treadgold	Plastic Propellants: The Influence of certain Ingredients and Adhesives on Propellant to Metal Bonds
17/M/59	WAC/92/15	R	A.J.B. Thomas & J.H.C. Vernon	The Theory of the E.R.D.E. Falling Cylinder Viscometer
1/R/60	WAC/116/01	U	B.M. Grieveson	The Glass Transition Temperature in Homologous Series of Linear Polymers
2/R/60	WAC/116/02	U	N.J. Blay, (Mrs) P.J. Fuller, J. Williams & R.L. Williams	The Structures of some Substituted Decaboranes and their Relation to Charge Distribution in Decaborane
4/R/60	WAC/116/03	U	R.P. Ayerst & R. Freelove	Crystallisation Studies: Rate of Growth of RDX Crystals from 55 per cent Nitric Acid Solution
6/R/60	WAC/116/06	U	E.L. Kendrew & J. Wenograd	A Photographic Study of the Impact Test
7/R/60	WAC/116/07	C	G.C. Bromberger, H.R. Broomhall, C.P. Conduit & A.J. Howard	The Stability of Colloidal Propellants: Part 3: High Impulse Compositions
11/R/60	WAC/91/30	C	G.W.C. Taylor & J.R. White	Lead Salts of 2,4-Dinitro-resorcinol: Part 3: Further Investigations of the Normal Salt; Development of R.D. 1337, Polymorphism, and Co-precipitated Delay Compositions
12/R/60	WAC/91/36	C	A.T. Betts, L.E. Dingle, R.H. Jones & A.W.H. Pryde	A New Continuous Process for TNT Manufacture: Part 2: Small Scale Pilot Plant and Considerations for Full Scale Design

Number	File	Classi-fication	Author	Title
13/R/60	WAC/91/37	R	I. Dunstan & J.V. Griffiths	The Reaction of Decaborane with Organometallic Reagents
14/R/60	WAC/91/38	U	L. Phillips	The Pyrolysis of Methyl Nitrite
3/M/60	WAC/117/03	C	-	A Short Survey of Current Processes for the Manufacture of TNT
4/M/60	WAC/117/04	R	Major S.MacM. Brown, R.A.O.C., J.K. Clark, D.A. Steel & P.D. Verschoyle	A Simple Mechanical Blast Meter for Comparative Measurement of Blast Effect

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Materials Research Reports and Technical Notes, Issued for D.M.X.R.D. Since 1.1.60

Classifications: R = RESTRICTED

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Number	Classi-fication	Author	Title
ADH/59/5	U	R.W. Bryant & W.A. Dukes	The Bonding of Threaded Joints: Part 4: Fpcxide, Polyester and Elastomeric Cements
CHEM/59/1	U	T.P. Hobin	Arsenical Polymers: Part 1: Attempts to Synthesise Polymers with Arsenic-to-Nitrogen Links in the Main Chain
CHEM/59/2	U	Idem	ditto Part 2: Synthesis of Poly(phenylene-arsines)
CHEM/59/3	U	J.H. Golden	The Development of Heat-resistant Polymers: Part 3: Preparation of Polymers Related to Poly-p-xylylene
RU/59/1	R	G.W. Harding & T.K. Overton	The Effect if Isopropyl Nitrate on Rubber and Plastics Materials
RU/59/2	U	R.W. Bryant & W.A. Dukes	The Kinetics of Crosslinking of a Polyphenyl/Formaldehyde Rubber
RU/59/3	U	Idem	The Physical Properties of a Polyphenol/Formaldehyde Rubber at Various Degrees of Crosslinking
RU/59/4	U	A.L. Stokoe	The Effect of Gasoline on some Physical Properties of Nitrile and Neoprene Rubber Vulcanizates
VAR/59/1	R	J. Wright	Replacements for Tung Oil in Air Drying Varnishes R.D.1177 and R.D.1281
VAR/59/2	R	Idem	The Protection of "Empty" Steel Ammunition in Storage by Stoving and Air Drying Varnishes
VAR/59/3	R	J. Gooding & J. Wright	Surface Coatings for Transportable Containers to Resist Liquid Monopropellants
PL/60/1	R	G.W. Harding & T.K. Overton	Demolition Slabs: Development of New Containers and Covering Materials: Part 1: Effect of Binder Oils on Films

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